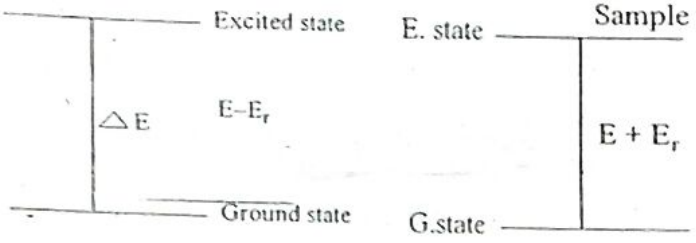
MOSSABAUER SPECTROSCOPY

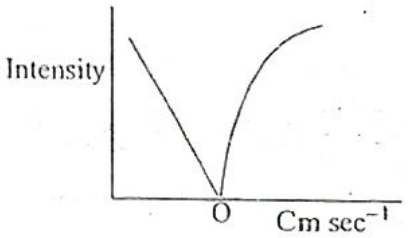
RECOIL ENERGY LOSS : When an exited nucleus emitted energy ΔE in the form of photon then a small part of this energy goes to used up in the kick back of the nucleus in a direction opposite to that of the photon. This small part of energy is known as recoil energy [Er]. The recoil energy is given by

$$E_r = \frac{E^2}{2mc^2}$$

$$E_r = \frac{536\,E^2}{m} eV$$

Dut to this recoil energy loss the residual energy ($E-E_r$) of the emitted photon is in adequate to re-exited a nucleus in the excited state.





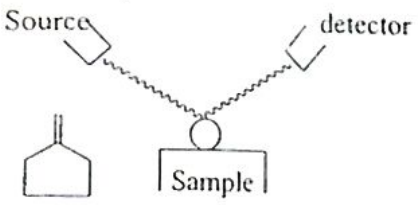
The re-absorption is possible only if the emitted photon has the excess energy. (E+Er) that it would be clearly absorb by another nucleus in the ground state.

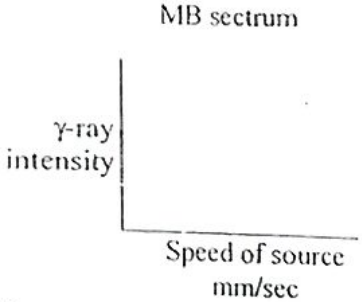
MOSSABAUER EFFECT : In 1958 R.L. Mossabaur given the brilliant suggestion to recover the recoil loss. That was to tide down the emitter and absorber atom in a molecule of high mass or to held them rigidly in a large crystal because the recoil energy. .

$$E_r \propto \frac{1}{\text{mass of emitter or absorber}}$$

By this procedure the recoil effect can be removed almost completely.
The doplar broading effect can be removed by cooling, the emitter and the absorber (source and sample). This is known as Mossbaur effect. (source and sample) and for this 1961 physics noble prize was given to this.

OBTAINING MB SPECTRA : It is obtained by moving the source towards or away from the fixed sample at a certain velocity and counting the γ - ray photon passing through the sample.





The Mossbaur spectrum is plot of speed of source against γ photon count or intensity.
The chemical shift is presented in the form of unit of speed (cm sec^{-1}) or mm/sec. or denoted by δ. The chemical shift is also known as isomer shift.

STANDARD : Generally single crystal of sodium nitro prusside is a standard absorber for Fe–57, ^{57}Fe – sod. nitro prusside ^{119}Sn – Ba stammate. If the same material is present at emitter and absorber than the chemical shift will be zero and the electronic environment or the electron density of the nucleus will decide the exact position of the chemical shift or any sample.

The e^- density in s orbital as a finite value at the nucleus. Therefore the electron in p, d and f orbital can effect the chemical shift only by screening the s electron from nuclear charge.

THE MOSSABAUER NUCLEI :

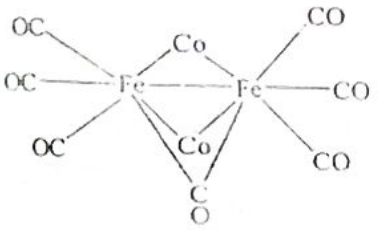
(1) The energy of γ radiation should be in the range of 10 – 200 Ke V,

(2) The half life of γ -emitter should be in the order of years. So that same source can be used for long time to get reproducible result of series of experiments.

(3) The conversion coefficient should be in high isotopic abundance. So that adequate sensitivity can be achieved.

Example: $Fe_2(CO)_9$

(1) ^{57}Fe



It will give only one signal.

1. About 18 nucleus are suitable all these above mentioned condition among these following are important. All are of odd mass.

^{57}Fe, ^{119}Sn , ^{129}Xe, ^{191}Ir, ^{61}Ni

$\equiv {}^{3}/_{2}$ $= {}^{1}/_{2}$

ENVIRONMENT OF Fe ATOM :

(1) Spherical symmetric → Td, O_h etc.

(2) Axial symmetric

(3) Assymmetric

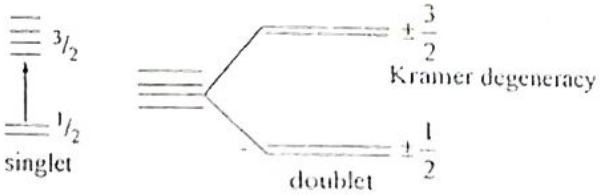
ML_6 – octahedral:

Spherical :

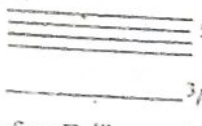
(1) Complete Octahedral (2) Complete tetrahedral (3) Complete Icosahedral.

If all ligand are same - spherical. If all ligand are not same - axisal symmetry one different.

If John teller distortion then axial symmetry.



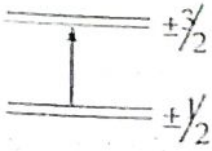
If assymmetric environment

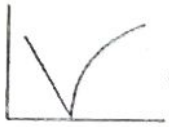


(1) Spin free Fe^{III} complex.

$3d^5$ spin free = $t_{2g}^3 . eg^2$ electronically spherical

If ligand symmetry is also spherical symmetrical then.

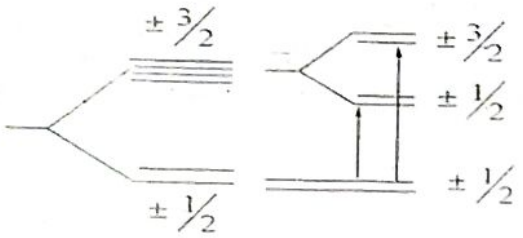


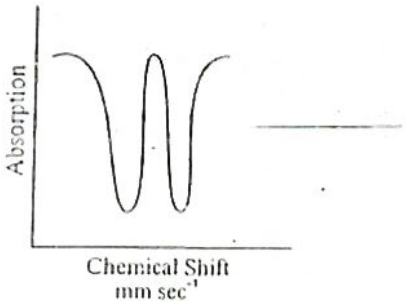


singlet only signal

(2) Spin paired Fe^{III} complex.

$3d^5 = t_2g^5\ eg^o \rightarrow$ axial symmetry





Selection rule $\Rightarrow \Delta I = 0, \pm 1$

(3) **Spin Free Fe^{II} complex :** $3d^6 = t_{2a}^4 eg^2$

- Axial electronic symmetry.
- Doublet in MB spectrum.

Example: $\left[Fe(H_2O)_7\right]SO_4$

(4) **Spin Paired Fe^{II} Complex :**

Spin paired Fe^{II} complex.

$t_{2a}^6\ eg^0 \rightarrow$ spherical

$\rightarrow$ Singlet in MB spectrum.

Example: $\left[K_4Fe(CN)_6\right]$ Singlet, Singlet

Example: $K_3\left[Fe(CN)_5NH_3\right] \rightarrow$ Doublet.

SOLVED PROBLEMS

1. The correct value of isomer shift (in Mossbauer spectra) and its explanation for Fe(II)–TPP and Fe(III)–TPP respectively from the following are: **[NET-June 2011]**
(TPP = tetraphenylporphyrinate)
(A) 0.52 mms^{-1} (B) 0.45mms^{-1}
(C) Increase in s electron density (D) Decrease in s electron density.
(a) (A) and (D); (B) and (C) (b) (A) and (C); (B) and (C)
(c) (B) and (D); (A) and (D) (d) (B) and (D); (A) and (C)

Soln. Both Fe(II)–TPP and Fe(III)–TPP are square planar (because of tetradentate-planar, porphyrine type ligand), and both Fe(II) and Fe(III) are dsp^2–hybridised, so there is s-electron density, which is responsible for their quadrupole moment and existence of mossbaue spectra.

So both Fe(II)-TPP and Fe(III)-TPP show increase in s-electron density, but Fe(II) has higher s–electron density. So Fe(II) has isomer higher shift (0.52 mms^{-1}) than Fe(III) (0.45 mms^{-1}).

Correct answer: (b)

2. In $^{57}Fe^*$ Mossbauer experiment, source of 14.4 keV (equivalent to 3.48×10^{12} MHz) is moved towards absorber at a velocity of 2.2 mm s^{-1}. The shift in frequency of the source for this sample is:
(a) 35.5 MHz (b) 25.5 MHz (c) 20.2 MHz (d) 15.5 MHz **[NET-Dec. 2011]**

Soln. Frequency shift $(\Delta\upsilon) = \frac{V\upsilon}{c}$; Where V = relative velocity of source and observer

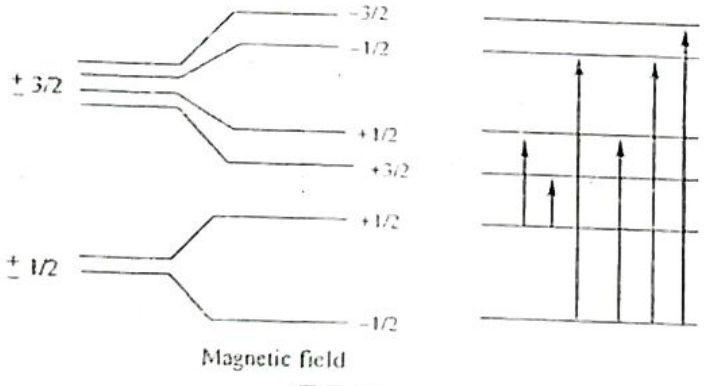
υ = frequency of emitted radiation

$$\therefore\ \Delta\upsilon = \frac{2.2\times10^{-3}\left(\frac{m}{s}\right)\times3.48\times10^{12}\,(Hz)}{3\times10^{8}\left(\frac{m}{s}\right)} = 2.55\times10^{7}\ Hz = 25.5\ mHz$$

Correct answer is (b)

3. If Mossbauer spectrum of $Fe(Co)_5$ is recorded in the presence of a magnetic field, the original spectrum with two lines changes into the one with **[NET-June 2012]**
(a) Three lines (b) Four lines (c) Five lines (d) Six lines

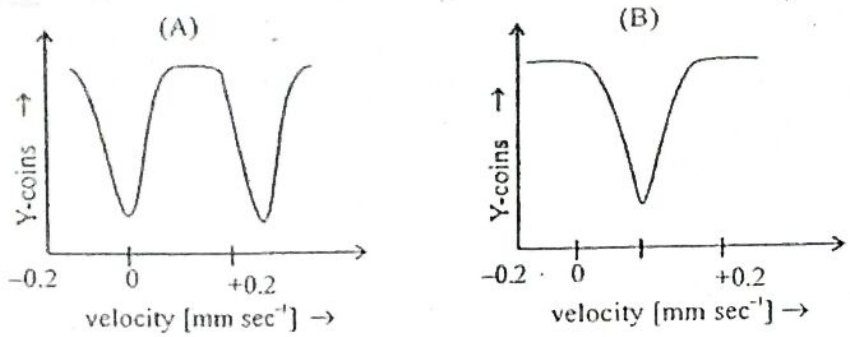
Soln.



Selection rule $\Delta M_I = 0, \pm 1$.

Correct answer is (d).

4. The Mossbauer spectra of two iron complexes are shown below. They may arise from (i) high-spin iron(III), (ii) high-spin iron(II) and (iii) low-spin iron(III) **[NET-June 2012]**



The correct matches of spectra (A) and (B) with the iron complexes are

(a) A with (i) and B with (ii) (b) A with (ii) and B with (i)

(c) A with (iii) and B with (ii) (d) A with (ii) and B with (iii)

Soln. (i) $Fe^{III} \rightarrow High-Spin-d^5 \rightarrow$ Spherical electronic configuration

$T_{2g}^5 E_g^2 \rightarrow$ No quadrupole splitting, singlet signal as shown in (B)

(ii) $Fe^{II} \rightarrow High-Spin-d^6 \rightarrow$ Axial electronic configuration

$T_{2g}^4 E_g^2 \rightarrow$ Quadrupole splitting, gives doublet signal as shown in (A)

(iii) $Fe^{III} \rightarrow Low-Spin-T_{2g}^5 E_g^0 \rightarrow$ Axial electronic configuration quadrupole splitting, doublet signal as shown in (A)

Correct answer is (b).

5. The recoil energy of a Mossabauer nuclide of mass 139 amu is 2.5 MeV. The energy emitted by the nucleus in keV is: **[NET-Dec. 2012]**

(a) 12.5 (b) 15.0 (c) 20.5 (d) 25.0

Soln. Recoil energy $R = \dfrac{\varepsilon_\gamma^2}{2Mc^2}$ $\qquad 2.5\times10^6 = \dfrac{536E_\gamma^2}{139\times931.5}$

Recoil energy $R = \dfrac{536\,E_\gamma^2}{M}$ eV $\qquad E_\gamma = \sqrt{\dfrac{2.5\times139\times931.5\times10^6}{536}} = 24.57\times10^3\,eV$

Correct answer is (d).

PHOTOELECTON SPECTROSCOPY

This spectroscopy is concered with forms of spectroscopy in which ionization of atom or molecule occur. The use of photons as energy source for ionization is basis of photo e^- spectroscopy. On the other hand use of high energy e^- for ionization of molecule is the basis of mass spectroscopy.

The P.E.S. lead to information about the difference in the energy between ground state molecule and their ion in a variety of electronic state. The techniques measures ionization energies and provide a direct picture of electronic energy levels.

The P.E.S is basically related to the photoelectric effect. There is thereshold frequency (υ_t) that requires to eject on e^- on the molecule. The work function ϕ is defined as minimum energy require to eject on e^-.

$$\phi = h\upsilon_t$$

and at higher frequency of the incident radiation the emitted e^- should have a kinetic energy i.e.

$$\text{KE} = \text{Incident}$$
$$= h\upsilon - h\upsilon_t \qquad \text{where } h\upsilon \text{ is incident radiation}$$
$$\text{K.E.} - = h(\upsilon - \upsilon_t)$$

Binding energy of e^- = $h\upsilon$ – K.E. = (work function)

PHOTOELECTRON SPECTRUM : It is a plot of binding energy against intensity of emitted electron or K.E. of electron against intensity.

Two types of photoelectron spectroscopy.

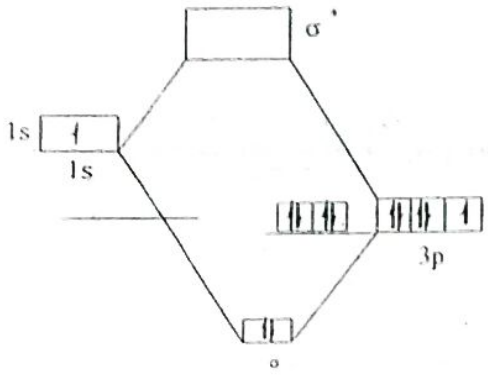
PES can be classified into two branches.

(Photoelectron spectroscopy for outershell UV-PES

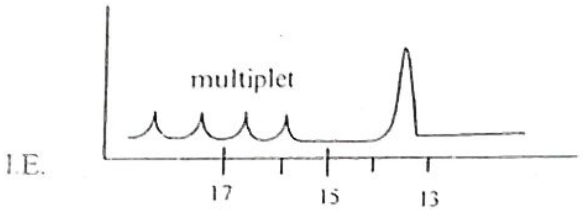
PES for inner shell X-ray

(1) The ionization energy of the outer e– of molecule and atom falls in the range 5 - 30ev and these electron can be studied by using vaccum ultraviolet radiation. UV. 200–400 nm range (2) Solid and liquid sample can be done and used but gas sample are mostly preffered.	(1) Core electron of atom and molecule have binding energies in the range of 100–10,000 eV energy and So these e– can be removed by using X-ray only. (2) Solid, liquid and gas sample can be used

PHOTOELECTRO SPECTRUM OF HCL



The photo electron spectrum of HCl is like this



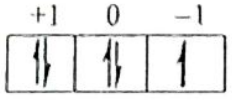
The bond at 13 e.v. is due to removed of nonbonded electron.
The bond at 16ev corresponds to removal of bonding electron In the removal of nonbonded e⁻ there is not change in Bond length. When bonding e⁻ are removed bond order and the bond length changes So we obtaine the vibrational fine structure.

Problem. Photoelectron Spectrum of Ar.

$1s, 1s^2, 2s^2, 2p^6, 3s^2, 3p^6$

G.S.Term Symbol = $3p^6$ $\quad {}^1S_0$

E.S. = Term Symbol $3p^5 + e^-$



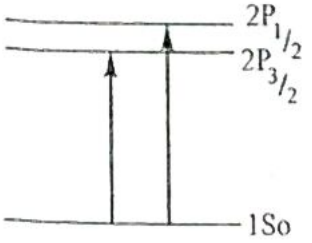
$^1s_0 \rightarrow {}^2P_{3/2}$ and $^2P_{1/2}$

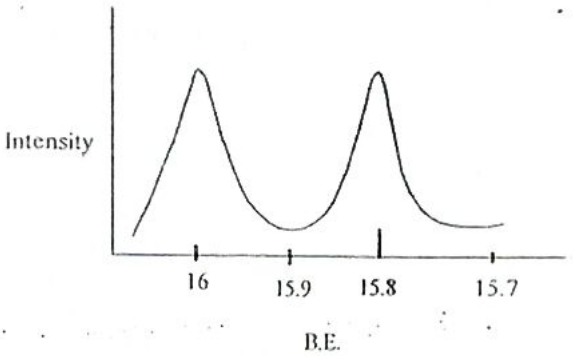
$^2P_{3/2}$ — Lower energy

$^2P_{1/2}$ — Higher energy

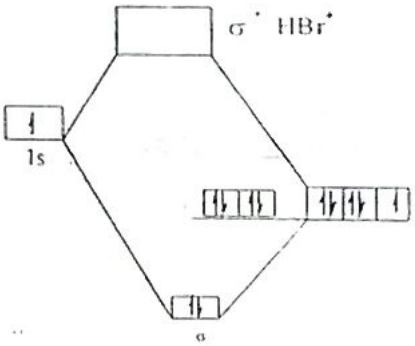
Transitions are

$^1s_0 \rightarrow {}^2P_{3/2}$, $^1s_0 \rightarrow {}^2P_{1/2}$

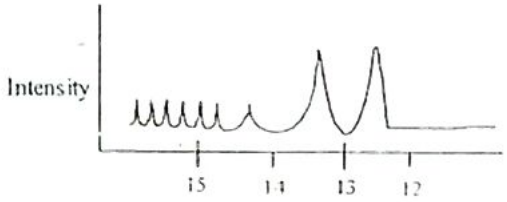




Problem. Photoelectron Spectrum of HBr.



Band at 12 eV doublet band is due to removal of non bonded e⁻ while band at 15 eV is removal of bonding electron.



The band at 12ev appears at doublet due to spin orbit coupling as follows. HBr has all paired electron in the G.S. But after ionization spin angular momentum = $-1/2$, or orbital angular momentum = 1

$2\pi_{3/2}$ $2\pi_{1/2}$

In HCl this band appear as a singlet because the magnitude of spin orbit coupling is very less.

magnitude of spin orbit coupling is HCl = 0.08 HBr = 0.33

HI = .66

Problem. How many peak will appear in U.V. photo electron spectrum and x-ray photo electron spectrum of.

(1) O_3 (2) N_3^-

AUGER EFFECT ONLY IN X-RAY: This is disadvantage of x-ray photoelectron spectroscopy

- X -ray photo e⁻ spectroscopy suffer from some secondary effect like flueorescence and other effect X-ray fluorescenece occure when hole created by the loss of core electron is filled up by another e⁻ of upper shell by emitting radiation in X-ray region.

And Auger effect occur when this x-ray is used up by a ground state molecule or ejection of another electron.

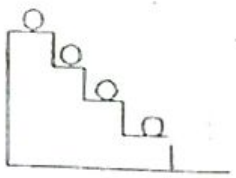
ROTATIONAL SPECTRA

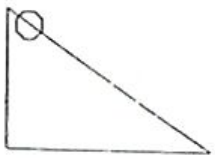
Region of the spectrum:
In increasing frequency of the regions are:

		ν	λ	E
1.	Radio frequency (used for broadcasting) (Study of reversal of nuclear spin and electronic spin)	$3\times10^{6}-3\times10^{10}$ *Hz*	10m–1cm	0.001–10 J/mol
2.	Microwave (Used for radar) (Study of transition between various rotational energy level) Rotational spectroscopy	$3\times10^{10}-3\times10^{12}$ *Hz*	1 cm–100μm	Hundreds of J/mol
3.	Infra-red region (Used for heating) (Study of transition between various vibrational energy level) (Vibrational spectroscopy)	$3\times10^{12}-3\times10^{14}$ *Hz*	100μm-1μm	upto the order of 10^{4} J/mol
4.	Ultraviolet and visible (Transition between electronic energy level's "electronic spectroscopy").	$3\times10^{14}-3\times10^{16}$ *Hz*	1μm-10μm	Hundreds of kilojoules/mole
5.	X-ray region (Energy changes involving the inner electron of an atom or molecule)	$3\times10^{16}-3\times10^{18}$ *Hz*	10 nm–100pm	Ten thousands and kilojoule.
6.	γ-rays region (Energy changes involving the rearrangement of nuclear particles)	$3\times10^{18}-3\times10^{20}$ *Hz*	100nm-1pm	$10^{9}-10^{11}$ per gram atom.

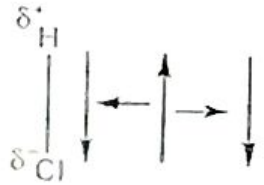
Structural information from molecular rotation.

rotational vibrational electronic nuclear	quantizedenergy levels
Translational	no selection rule

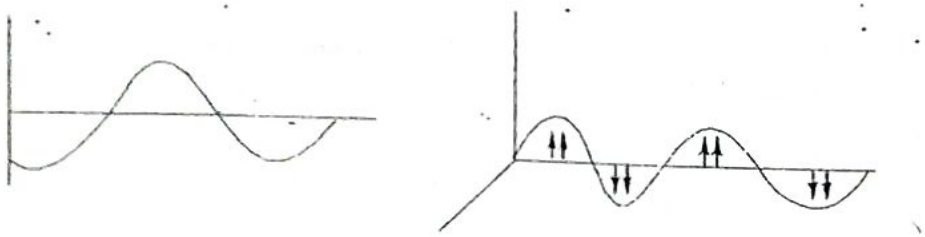




Microwave activity: For a molecule to be microwave active it should have permanent dipole moment.



dipole is a vector quantity microwave radiation are electro magnetic radiation.



Fluctuating electric pole

- A molecule like HCl have a permanent electric dipole moment and if we rotate the molecule from the centre of gravity its $+\delta$ and $-\delta$ charges places periodically and the component dipole moment in a given direction fluctuate regularly.
  When the frequency of this fluctuating dipole becomes equal to the frequancy of microwave region the energy can be absorb.
  If there is no permanent dipole in the molecule like Cl_2, H_2 no interaction will and this type of molecule will be microwave inactive.

- Depend on the moment of inertia on different axis.

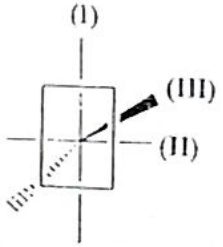
  $I = \Sigma m_i r_i^2$

  $I = m_1r_1^2 + m_2r_2^2 + m_3^2r_3^2$.....

For the purpose of studing rotation spectra in a molecule we have to classify the molecule according to principal moment of inertia.

The moment of inertia (I) of any molecule about any axis is given by this moment of inertia through centre of gravity.

There is one of these axis is labelled as C-axis about which moment of inertia has its maximum value



and the IInd axis is labelled axis A-axis about which the moment of inertia has minimum value.

A and C axis must be usually perpendicular these together with a IIIrd axis the B-axis which is perpendicular to the other two are called the principle axis of inertia. Molecule may be divide into 3 catagory generally.

(a) Spherical

(b) Symmetrical

(i) Oblate and (ii) Prolate

(c) Non-symmetrical

(a) In spherical:

$I_A = I_B = I_C$ (CH_4, SF_6)

In oblate, $I_C > I_A = I_B$ (C_6H_6) (I_C is always greater value than I_A and I_B)

In Prolate, $I_C = I_B > I_A$ (CH_3I)

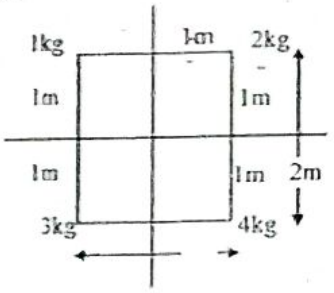
In Non-symmetrical $I_A \neq I_B \neq I_C$ (HCHO)

C = Principle axis because here I_C has maximum value that is why it is principle axis. where, I_A, I_B and I_C meet that point is called principle axis.

$$I_{xx} = \Sigma m\left(Y_{cy} - Z_{xy}\right)^2$$

$$I_{yy} = \Sigma m\left(Z_{xy} - X_{zy}\right)^2$$

$$I_{zz} = \Sigma m\left(X_{yz} - Y_{cz}\right)^2$$



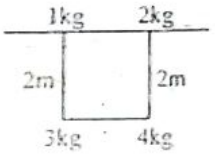
$I = m_1r_1^2 + m_2r_2^2 + m_3r_3^2 + m_4r_4^2$

$m_1 = 4kg$, $m_2 = 2kg$, $m_3 = 3kg$, $m_4 = 1kg$

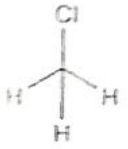
$r_1 = 1m$ $r_1 = 1m$ $r_1 = 1m$ $r_1 = 1m$

$$= 4\times(1)^2 + (2)\times(1)^2 + 3\times(1)^2 + (1)\times(1)^2 = 4+2+3+1$$

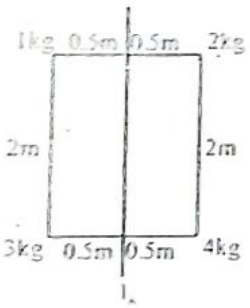
$\boxed{I_B = 10}$ kg – m^2



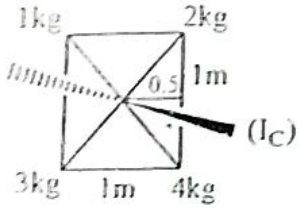
$$I = 4\times(2)^2 + 3\times(2)^2 + 2\times 0^2 + 1\times 0^2 = 4\times 4 + 3\times 4 = 16+12 = 28$$



→ (When we put this axis. So, Cl and H value is zero)



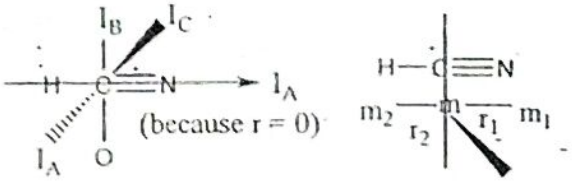
$$I_A = 1\times(0.5)^2 + 2\times(0.5)^2 + 3\times(0.5)^2 + 4\times(0.5)^2$$
$$= 0.25 + 0.75 + 0.50 + 1 = 2.5\ \text{kg} - \text{m}^2$$



$$I = 4\times\left(\sqrt{1.25}\right)^2 + 2\times\left(\sqrt{1.25}\right)^2 + 3\times\left(\sqrt{1.25}\right)^2 + 1\times\left(\sqrt{1.25}\right)^2$$
$$I = 5 + 2.5 + 3.75 + 1.25 = 12.5$$

$\boxed{I_C = 12.5}$ It is I_C because the I value is maximum.

For linear molecule:



$I_B = I_C \qquad (I_A = 0)$

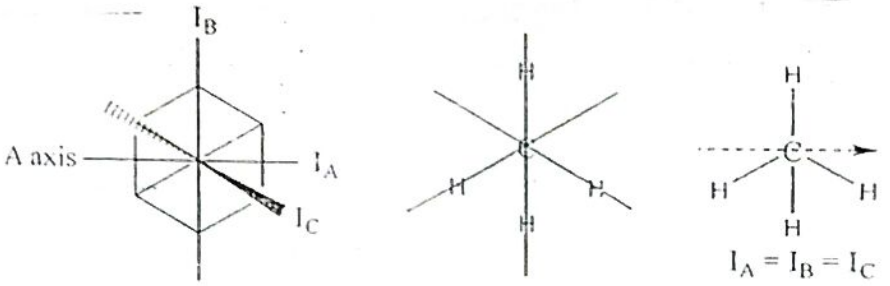
$I = m_N r_{CN}^2 + m_H r_{CN}^2$

- For a linear molecule such as H—C≡N

  $I_C = I_B > I_A \quad \& \quad I_A = 0$
- For a symmetric top molecule two of the principle moment of inertia are equal and IIIrd is not zero.
- $I_C = I_B > I_A \rightarrow$ Prolate

  The best example of prolate symmetric molecule is Methyl iodide CH_3I, CH_3Cl.
- Since the heavy iodine nucleus makes no contribution to I_A. It is k/as prolate symmetric rotator.
- If $I_C > I_B = I_A$ then it is known as Oblate Symmetric.

  The best example of Benzene.



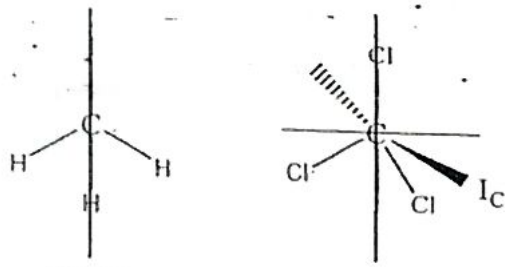
- A symmetric rotator must have either C_n axis with $n > 2$ or $n \geq 2$ or S_4 axis.
- CH_3I has C_3 axis $\rightarrow$ symmetric (Prolate)
- Bezene has C_6 axis $\rightarrow$ Symmetric (Oblate)
- Allene has S_4 axis $\rightarrow$ Symmetric Prolate.
- A spherical rotator has all 3 principle moment of inertia is equal $I_A = I_B = I_C$.
- In case of methane and SF_6 they belong to O_h to Td symmetry. So, they ae spherical rotator and asymmetric rotator has all the moment of inertia. $I_A \neq I_B \neq I_C$

  e.g. formaldehyde.
- For many assymetric rotator

  $\boxed{I_c = I_b > I_a}$

  I_C and I_B has no more difference
- There are k/as prolate near symmetric rotator.

  $I_C > I_a = I_b$
- Classify BCl_3 and CH_3I as an oblate and prolate symmetric.



Prolate
symmetric

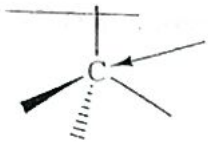
BCl_3 as coplanar molecule the center of mass of BCl_3 sites at central Boron atom there for one of the principle axis is perpendicular to the molecular plane other two axis lie in the plane of molecule.

The unique axis that is perpendicular to the plane of the molecule all three chlorine atom lie as far as possible from the axis. So, the moment of inertia about this axis is maximum. So, it is an example of Oblate top symmetrical molecule.

When all mass in come on the axis than I becomes zero.

Than, I = 0

whole molecule cut by axis.



centre of gravity is always +ve in the centre. Centre of gravity never break.

- In complicated system I is dependent on θ also.

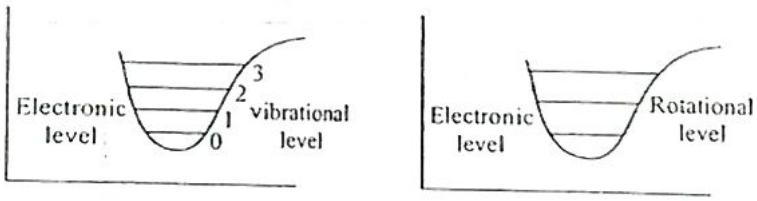
$$I = \mu r^2$$

How rotational spectra generated:

Dipole moment must be there

- Magnetic moment should be different than dipole moment +ve.
- If magnetic moment is same than dipole moment not present. So, it become Microwave inactive.

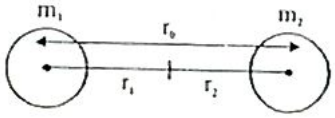
$$\underbrace{I_A = I_B = I_C}_{\text{Microwave inactive spherical}}$$



$$I = \mu r^2$$

$$E = \frac{1}{2}\omega^2$$

$$E = BJ(J+1)$$



$$I = \frac{1}{2}\left[m_1 v_1^2 + m_2 v_2^2\right]$$

$v_1 = r_1\omega \qquad \Rightarrow v_2 = r_2\omega$

$$I = \frac{1}{2}\left[m_1r_1^2\omega^2 + m_2r_2^2\omega^2\right] = \frac{1}{2}\omega^2\left(m_1r_1^2 + m_2r_2^2\right)$$

$$\boxed{I = \frac{1}{2}I\omega^2}$$

Rotational kinetic energy

$L = I\omega \qquad \Rightarrow L = mvr = mr\omega r.$

$\boxed{I = \mu r^2}$ (centre of gravity)

The molecular rotate about a point 'c' the centre of gravity this is defined by the moment or balancing the centre of mass condition i.e. $m_1r_1 = m_2r_2$

$$I = m_1r_1^2 + m_2r_2^2 = m_1r_1r_1 + m_2r_2r_2 \qquad \Rightarrow \boxed{I = (m_1 + m_2)r_1r_2}$$

r_1 and r_2 may be calculated in the form of r_0.

$m_1r_1 = m_2r_2 \qquad$ Put $r = r_0 = r_1 + r_2,\ r_2 = r_0 - r_1$

$m_1r_1 = m_2(r_0 - r_1)$

$$\boxed{r_1 = \frac{m_2r_0}{m_1 + m_2}}$$

$m_2r_2 = m_1r_1 \qquad \Rightarrow m_2r_2 = m_1(r_0 - r_2)$

$$\boxed{r_2 = \frac{m_1r_0}{(m_1 + m_2)}}$$

$I = (m_1 + m_2)r_1r_2$

Put the value of r_1 and r_2 in above equation

$$I = \frac{m_1m_2r_0^2}{(m_1 + m_2)} \qquad \Rightarrow I = \mu r_0^2$$

$$E = \frac{1}{2}I\omega^2 \qquad \rightarrow \left(\frac{2E}{I} = \omega^2 \quad \Rightarrow \omega = \sqrt{\frac{2E}{I}}\right)$$

$L = I\omega$ ...(i)

Put the value of ω in equation (i)

$$L = I\sqrt{\frac{2E}{I}} \qquad \Rightarrow L = \sqrt{2EI} \qquad \text{... (ii)}$$

$$\boxed{E_J = \frac{h^2}{8\pi^2I}J(J+1)} \text{ joule}$$

Put the value of E_J in equation (ii)

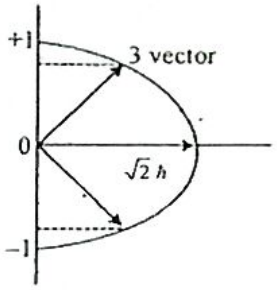
$$L = \sqrt{\frac{2Ih^2}{8\pi^2I}J(J+1)} = \sqrt{\frac{h^2}{4\pi^2}}\sqrt{J(J+1)} \qquad \Rightarrow \boxed{L = h\sqrt{J(J+1)}}$$

Problem: Find a vector diagram of an angular momentum having value $\omega = \sqrt{2}\,\hbar$.

$J = \ell + s, \qquad J = \ell$

$\sqrt{J(J+1)}\hbar = \sqrt{2}\hbar \qquad J = 1$

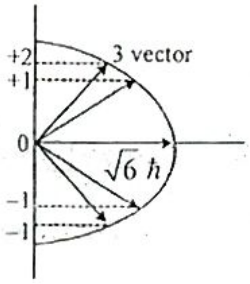
$\ell = 1 \quad (m_\ell = -1, 0, +1)$



If J = 1 (3 fold degenerate)

$\sqrt{6}\hbar, \quad \sqrt{J(J+1)} = \sqrt{6}\,\hbar \qquad (J = 2)$

$m_J = +2, +1, 0, -1, -2$



$\boxed{J = 2 \Rightarrow \text{five fold degenerate}}$

If $J = 3 \Rightarrow 7$ fold degenerate

$$E = \frac{h^2}{4\pi^2 I} \qquad \Rightarrow \left[E = \frac{h^2}{8\pi^2 I} J(J+1)\right]$$

Put the value of E in above.

$$\frac{h^2}{8\pi^2 I} J(J+1) = \frac{h^2}{4\pi^2 I} \quad \Rightarrow J(J+1) = 2; \quad J(J+1) = 2; \quad 2J + J = 2 \qquad \boxed{J = 1}$$

By the use of schrodinger wave equation, rotation energy levels allowed to the rigid diatomic molecule are giving by the expression

$$\boxed{E_J = \frac{h^2}{8\pi^2 I} J(J+1)} \text{ joule}$$

Rigid rotor means centrifugal rotation is not positive.

fixed in rigid rotor
(centrifugal force)

$$E = \frac{E_J}{hc} = \frac{h^2}{8\pi^2 I}\frac{\hat{\lambda}}{hc} J(J+1) \Rightarrow \boxed{E = \frac{h}{8\pi^2 Ic} J(J+1)}\ \text{cm}^{-1} \qquad \left[I = \mu r^2 = \frac{m_1 m_2}{m_1 + m_2} r^2\right]$$

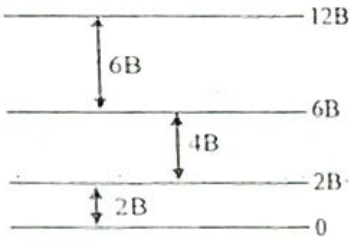
$\boxed{E = BJ(J+1)\ \text{cm}^{-1}}$ Where, B = Rotational constant $\qquad \left[B = \frac{h}{8\pi^2 Ic}\right]$

$J = 0 \quad E_0 = B\times 0(0+1) \quad \Rightarrow \boxed{E_0 = 0}$

$J = 1 \quad E_1 = B\times 1(1+1) \quad \Rightarrow \boxed{E_1 = 2B}$

$J = 2 \quad E_2 = B\times 2(2+1) \quad \Rightarrow \boxed{E_2 = 6B}$

$J = 3 \quad E_3 = B\times 3(3+1) \quad \Rightarrow \boxed{E_3 = 12B}$



The energy difference between continuous energy level J and J + 1 is J and (J+1)

$$\Delta E = E_{J+1} - E_J = B(J+1)(J+1+1) - BJ(J+1) = B(J+1)(J+2) - BJ(J+1)$$

$$= BJ(J+1) + 2B(J+1) - BJ(J+1)$$

$$\Delta E = 2B(J+1)$$

$0 \rightarrow 1 \quad J = 0 \quad \boxed{\Delta E = 2B(0+1) = 2B}$

$1 \rightarrow 2 \quad J = 1 \quad \boxed{\Delta E = 2B(1+1) = 4B}$

$2 \rightarrow 3 \quad J = 2 \quad \boxed{\Delta E = 2B(2+1) = 6B}$

At J = 0, we have $E_J = 0$

- It means the molecule is not rotating at all
- J = 1, $E_1 = 2B$ molecule rotate and it has its lower angular
- We may continue to calculate E_J with increasing value. There is a no limit of calculation of E_J value

In practice there come a point where the centrifugal force of a rapidly rotating diatomic molecule is greater than the strength of the bond. This molecule is disrupted. Generally this point is not reached at normal temperature.

SOLVED PROBLEMS

1. The moment of inertia of CO molecule is 1.46×10^{-46} kg m^2. Calculate the energy in electron volt and angular velocity in the lowest energy level of the CO molecule.

Soln. J = 1 (lowest energy from where rotation start.

$$E = \frac{h^2}{8\pi^2 I} J(J+1) = \frac{h^2}{8\times\left(\frac{22}{7}\right)^2 \times 1.46\times10^{-46}} \times 1(1+1) = \frac{\left(\left(6.6\times10^{-34}\right)^2\right)^2 \times 10^{46}}{8\times22\times1.46} \times 2\times1.6\times10^{-19}$$

$$E = 4.7\times10^{-4}\ \text{eV} \qquad \Rightarrow E = \frac{1}{2} I\omega^2$$

$\Rightarrow \quad \omega = \sqrt{\frac{2E}{I}} \quad \Rightarrow \omega = \sqrt{\frac{2\times 7.6\times 10^{-23}\,J}{1.46\times 10^{-46}\,kg-m^2}}$ $\qquad J = N-m = kg\,\frac{m}{sec^2}$

$I = \frac{kgm^2}{sec^2}$

$\omega = \frac{1}{sec} \quad \Rightarrow \quad \boxed{\omega = 1\times 10^{12}\,sec^{-1}}$

$\Rightarrow \quad \omega = 2\pi\nu; \; \nu = \frac{\omega}{2\pi} = \frac{1\times 10^{12}}{2\times 3.14}$

$\Rightarrow \quad \nu = 0.159\times 10^{12} \quad \Rightarrow \boxed{\nu = 1.5\times 10^{11}}$

2. If $J = 0 \rightarrow J = 1$

Assorption line in CO occurs at a frequency = 1.153×10^{11} cycles/sec. Calculate the moment of inertia and internuclear separation of CO molecule.

$\nu = \frac{\omega}{2\pi} \quad \Rightarrow \quad \omega = 2\pi\nu = 2\times 3.14\times 1.153\times 10^{11} = 7.290\times 10^{11}$

$J = 0 \rightarrow J = 1 \qquad \Delta E = B(J+1) = B(1+1)$

$\Delta E = 2B \quad \Rightarrow \Delta E = \frac{2h^2}{8\pi^2 I}$

$(\Delta E = h\nu) \quad \Rightarrow \quad h\nu = \frac{2h^2}{8\pi^2 I} \quad \Rightarrow I = \frac{2h}{8\pi^2\nu} \quad \Rightarrow I = \frac{h}{4\pi^2\nu} \approx 10^{-46}$

$\nu = 1.153\times 10^{11}$ cycle / sec

$I = \mu r^2 \quad \Rightarrow m_{CO} = \frac{m_c m_0}{m_c + m_0} = \frac{12\,\frac{gm}{mol}\,16\,\frac{gm}{mol}}{12\,\frac{gm}{mol} + 16\,\frac{gm}{mol}}.1\,mole = \frac{(12\times 16)}{12+16}\,\frac{gm}{mol}$

$= \frac{48}{7}\,\frac{gm}{mole} = \frac{48\times 10^{-3}}{7\times 6.023\times 10^{23}}(molecule)$

$= \frac{48}{7}\times 1.67\times 10^{-27} = \frac{80.16}{7}\times 10^{-27}$

$\boxed{\mu_{CO} = 11.45\times 10^{-27}}$

gm/mol to convert into kg/mol multiply by and this is used in reduce mass.

$I = \mu r^2 \quad \Rightarrow r = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{10^{-46}}{11.46\times 10^{-27}}} = \sqrt{\frac{0.087\times 10^{-19}}{1000}} = \sqrt{87\times 10^{-16}}$

$r = 9.32\times 10^{-8} = 0.93\times 10^{-9}$

$J = \pm 1 \rightarrow$ vibrational

The transition can occur from a particular level to its immediate neighbour either above or below, we consider only transition when J changes by one unit. All other transition spectroscopically forbidden transition such as result is called selection rule and a rigid diatomic rotator $J = \pm 1$

The transition intensity is proportional to the square of transition moment which is given by

$$\boxed{R_r = \int \psi'^{*} \mu \psi'' d\tau}$$

R_r = transition moment

μ = dipole moment (μ must be zero)

$$\boxed{I \propto Rr^2}$$

If $\mu = 0$ than transition moment become zero. If transition moment is zero than intensity is also zero. So, μ never be zero.

If we change $\Delta J = \pm 2, \pm 3$ than it is forbidden. The transition probability for all these changes become zero.

So, rotational selection rule constitute a condition for which the intensity $R_r \neq 0$.

The molecule must have a parmanent dipole moment $(\mu \neq 0)$

$\Delta J = \pm 1$, otherwise transition probability is zero (according to Schrodinger)

Relative Population of differnet energy levels:

That may be calculated by Boltzmann distribution laws

$$n_i = g_i e^{-E_i/RT}$$

Where, g_i = degeneracy

n_i = molecule in ith level

T = temperature.

$$N_J = g_J e^{-E_J/RT}$$

$$N_0 = g_0 e^{-E_0/RT}$$

$g_0 = 1$, $E_0 = 0$

$$\Rightarrow \quad N_0 = 1 e^{0} \quad \Rightarrow \boxed{N_0 = 1}$$

$$\frac{N_1}{N_0} = \frac{g_1 e^{-E_J/kT}}{g_0 e^{-E_0/kT}} \qquad (g_J = \text{degeneracy}, g_J (2J+1)$$

$$\frac{N_J}{N_0} = (2J+1) e^{-E_J/kT} \qquad \left[E_J = B_J (J+1)\right]$$

Put the value of E_J in above equation.

$$\boxed{\frac{N_J}{N_0} = (2J+1) e^{-B_J(J+1)/kT}}$$

N_J = Number of mole in J_{th} level.

$$\boxed{B = \frac{h}{8\pi^2 I_C}} \Rightarrow E_J \rightarrow cm^{-1}$$

Multiply by hc

$$\boxed{\frac{N_J}{N_0} = (2J+1) e^{-Bhc J(J+1)/kT}}$$

We may calculate the ratio of number of molecule in first level and zero level at room temperature, T = 300K

The relative population in (J + 1) state is $\frac{N_1}{N_0}$ taking B = 2 cm^{-1}.

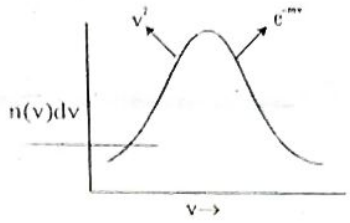
$$\frac{N_1}{N_0} = (2J+1)\,e^{-BhcJ(J+1)/RT}$$

$$= (2\times1+1)\,e^{-\frac{2cm^{-1}\times6.6\times10^{-34}\times3\times10^{10}\times1(1+1)}{1.38\times10^{-23}\times300}} = 3\,e^{-\frac{79.2\times10^{-24}\times10^{23}}{414}} = 3\,e^{-(0.191)\times10^{-1}} = 3\,e^{-0.019}$$

Maxwell distribution law:

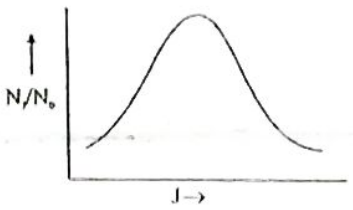
$$n(v)dv = 4\pi N\left(\frac{m}{2\pi kT}\right)^{3/2}$$

$$v^2 e^{-mv^2/kT}dv$$



When we plot a graph between $\frac{N_1}{N_0}$ increases at low J untill, at higher J, the exponetial factor dominate at $\frac{N_J}{N_0}$ decreases.

There are two opposing factor between $\frac{N_J}{N_0}$ (2J + 1) and $e^{-BJ(J+1)/kT}$ (2J + 1) factor increases with J and $e^{-BJ(J+1)/kT}$ factor decreases with increases J.



$$\frac{N_J}{N_0} = (2J+1)\,e^{-BJ(J+1)hc/kT}$$

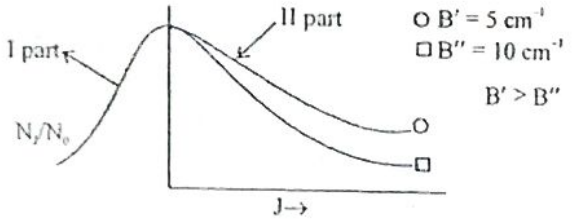
Maximum population may be calculated by using Maxima minima condition i.e. first differentiation of $\frac{N_1}{N_0}$ w.r.t. $d_J\left(\frac{d(N_J/N_0)}{d_J} = 0\right)$

$$\Rightarrow \quad \frac{d(N_J/N_0)}{d_J} = 0 \qquad \Rightarrow J_{max} = \sqrt{\frac{kT}{2Bhc}} - \frac{1}{2} \qquad \Rightarrow \boxed{J_{max} = \sqrt{\frac{kT}{2B}} - \frac{1}{2}}$$

$$\Rightarrow \quad B = \frac{h}{8\pi^2 Ic} \qquad \Rightarrow B = \frac{h}{8\pi^2 \mu r^2 c}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \text{(reduce mass)}$$

Another factor may be the effect of rotational constant B rapid decrease of N_J/N_0 with increasing J with larger B.



- Third factor also there i.e. dependent on first factor $g_j = 2JH$
- First part of the graph increases if g_j increases.

Effect of Isotopic substitution:

In a particular atom in a molecule is replace by its isotope, no appriciable change in internuclear distance on isotopic substitution. A change in total mass occur hence its moment of inertia changes and value of B changes.

$$B = \frac{h}{8\pi^2 Ic} \qquad I = \mu r^2 \rightarrow \text{heavier}$$

$$B = \downarrow \qquad I = \uparrow$$

The spectrum of heaviour species will show smaller separation between the lines then that of lighter one. It was found by Gillman Etal.

They found that if we takes

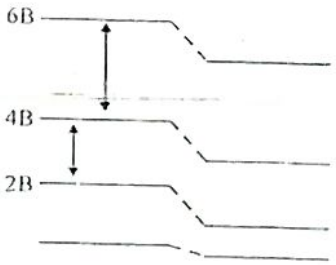
$^{12}C \quad ^{16}O = 3.84$

$^{13}C \quad ^{16}O = 3.67$

$$\frac{B}{B'} = \frac{\frac{h}{8\pi^2 I_C}}{\frac{h}{8\pi^2 I'_C}} = \frac{I'}{I} = \frac{\mu' r^2}{\mu r^2} = \frac{\mu'}{\mu} \Rightarrow \boxed{\frac{B}{B'} = \frac{\mu'}{\mu}}$$

B = rotational constant before isotopic substitution

B' = rotational constant after isotopic substitution



3. $J = 0 \rightarrow J = 1$

Rotational absorption of light occur at 1.153×10^{11} sec^{-1} in ^{12}C ^{16}O at 1.102×10^{11} cycles/sec in $^{*}C$ ^{16}O. Calculate the mass number of unknown $^{*}C$.

Soln. $\frac{B}{B'} = \frac{\mu'}{\mu}$

$E = h\nu = BJ(J+1) \quad \Rightarrow E = h\nu' = B'J(J+1)$

$$\frac{h\nu}{h\nu'} = \frac{BJ(J+1)}{BJ'(J+1)} \quad \Rightarrow \frac{\nu}{\nu'} = \frac{B}{B'} = \frac{\mu}{\mu'}$$

$$\frac{\nu}{\nu'} = \frac{\mu'}{\mu} \qquad \Rightarrow \mu' = \frac{m^* \times 16}{m^* + 16} \times 1.67 \times 10^{-27}$$

$$\mu = \frac{16 \times 12}{16+12} \times 1.67 \times 10^{-27} = \frac{320.64 \times 10^{-27}}{20} \quad \Rightarrow \mu = 11.45 \times 10^{-27}$$

$$\frac{1.153 \times 10^{-11}}{1.102 \times 10^{-11}} = \frac{\mu'}{11.45 \times 10^{-27}} \qquad \Rightarrow \mu' = 11.45 \times 10^{-27} \times 1.045 = 11.979 \times 10^{-27}$$

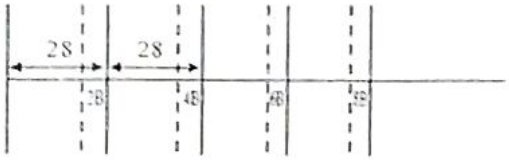
$$\mu' = \frac{m^* \times 16}{m^* + 16} \times 1.67 \times 10^{-27} \qquad \Rightarrow 11.979 \times 10^{-27} = \frac{m^* \times 16}{m^* + 16} \times 1.67 \times 10^{-27}$$

$$(m^* + 16)7.17 = m^* \times 16 \qquad \Rightarrow 7.17m^* + 16 \times 7.17 = m^* \times 16$$

$$7.17m^* - m^* 16 = -114.77 \qquad \Rightarrow -m^* 16 + 7.17m^* = -114.77 \qquad \Rightarrow m^* = \frac{114.77}{8.83}$$

$$\boxed{m^* = 12.99 \approx 13}$$

4. The spacing of series of lines in the microwave region of $H^{79}Br$ is 17 cm^{-1} apart. Find the internuclear distance



$2B = 17\ cm^{-1} \qquad \Rightarrow B = 8.5\ cm^{-1}$

$$B = \frac{h}{8\pi^2 Ic} = \frac{h}{8\pi^2 \mu r^2 c}$$

$$\mu = \frac{m_H m_{Br}}{m_H + m_{Br}} \times 1.67 \times 10^{-27}\ kg/molecule$$

$$= \frac{1 \times 79}{1+79} \times 1.67 \times 10^{-27}\ kg/molecule = \frac{131.93 \times 10^{-27}}{80} \qquad \Rightarrow \mu = 1.64 \times 10^{-27}$$

$$I = \frac{h}{8\pi^2 Bc} = \frac{6.6 \times 10^{-34}}{8 \times (3.14)^2 \times 8.5 \times 3 \times 10^{10}} = \frac{6.6 \times 10^{-34}}{2011.35 \times 10^{10}} \qquad \Rightarrow I = 0.00328 \times 10^{-44}$$

$$\Rightarrow r = \sqrt{\frac{0.0032 \times 10^{-44}}{1.64 \times 10^{-27}}} = \sqrt{0.00200 \times 10^{-17}} = \sqrt{2.0 \times 10^{-17} \times 10^{-17}} \qquad r = 1.41 \times 10^{-10}$$

$$= \sqrt{2} \times 10^{-20} \qquad \boxed{r = 1.41\text{Å}}$$

5. The most population rotational state for HCl ($B = 8.5\ cm^{-1}$) at 300K is

(a) 2 (b) 3 (c) 5 (d) 7

Soln. $J_{max} = \sqrt{\frac{kT}{2Bhc}} - \frac{1}{2} = \sqrt{\frac{1.38\times10^{-23}\times300}{2\times8.5\times6.6\times10^{-34}\times3\times10^{10}}} - \frac{1}{2}$

$$= \sqrt{\frac{414\times10^{-23}\times10^{24}}{337.92}} - \frac{1}{2} = \sqrt{1.22\times10} - \frac{1}{2} = 3.5 - \frac{1}{2} = 3.5 - 3.5 = 3$$

$$\boxed{J_{max} = 3}$$

6. The population of Jth rotational level N_J is given by

$$N_J = N_0(2J+1)\,e^{-BJ(J+1)/kT}$$

Soln. The J_{max}

$$J_{max} = \sqrt{\frac{kT}{2Bhc}} - \frac{1}{2} \quad \Rightarrow J_{max} = \sqrt{\frac{kT}{2B}} - \frac{1}{2}$$

$$\boxed{J_{max} = \frac{\sqrt{\frac{2kT}{B}} - \frac{1}{2}}{2}}$$

7. The spacing between the rotational line of HF is $40\ cm^{-1}$.

DF → Rotational line

$2B = 40\ cm^{-1}$

$$\frac{B}{B'} = \frac{\mu'}{\mu} \quad \Rightarrow 2B' = \frac{\mu_{HF}\times 2B}{\mu_{DF}}$$

$$\mu_{HF} = \frac{1\times19}{1+19} = \frac{19}{20} \quad \Rightarrow \mu_{DF} = \frac{2\times19}{2+19} = \frac{38}{21}$$

$$\frac{\mu_{HF}}{\mu_{DF}} \approx \frac{1}{2} \quad \Rightarrow 2B' = \frac{1}{2}\times40$$

$$\boxed{2B' = 20\ cm^{-1}}$$

8. Calculate the frequency of wave number for the first rotational transtion $J = 0 \rightarrow 1$ in $D^{35}Cl$. The D–Cl bond length = 125 pm, $\bar{\nu} = ?$

Soln. $\mu = \frac{2\times35}{2+35}\times1.67\times10^{-27} = \frac{70}{37}\times1.67\times10^{-27}$

$$I = \mu r^2 = \frac{70}{37}\times(125)^2\times(10^{-12})^2 = 29560.8\times10^{-24}\times1.6\times10^{-27} = 47297.28\times10^{-51}$$

$E = h\nu \quad \Rightarrow \nu = c\bar{\nu}$

$E = hc\bar{\nu} = BJ(J+1)$ (for $J = 1$)

$\Delta E = hc\bar{\nu} = 2B$

$\Delta E = \bar{\nu} = 2B$

$\left(B = \frac{h}{8\pi^2 I_C}\right)$

$$\bar{\nu} = 2B = \frac{2h}{8\pi^2 I_C}$$

$\left(B = \frac{h^2}{8\pi^2 I}\right)$ $\Rightarrow hc\Delta E = \frac{2h^2}{8\pi^2 I}$

$$\bar{v} = \frac{2h}{8\pi^2 I_C} = \frac{2\times 6.626\times 10^{-34}}{8\times(3.14)^2\times 47297.28\times 10^{-51}} = \frac{13.24\times 10^{-34}\times 10^{43}}{236.63\times 47297.28} \approx \frac{13.24\times 10^{9}}{11191974.2}$$

$$\bar{v} = \frac{0.00000118\times 10^{9}}{10^{6}} = 1.1\times 10^{3}$$

9. What are the degeneracy of the following diatomic rotational energy leve.

(i) 0 (ii) $\frac{h^2}{I}$ (iii) $\frac{6h^2}{I}$

Soln. (i) $E = \frac{h^2}{8\pi^2 I}J(J+1)$ $\left(h = \frac{h}{2\pi}\right)$

$E = \frac{h^2}{2I}J(J+1)$ $\Rightarrow 0 = \frac{h^2}{2I}J(J+1)$ $\Rightarrow 0 = \frac{h^2}{2I}J(J+1)$ $\Rightarrow 0 = J(J+1)$

$[J = 0]$ $\Rightarrow \boxed{g_J = 2J+1 = 2\times 0+1}$ $\Rightarrow \boxed{g_J = 1}$ · (nondegenerate)

(ii) $E = \frac{h^2}{2I}J(J+1)$ $\Rightarrow \frac{h^2}{I} = \frac{h^2}{2I}J(J+1)$

(iii) $E = \frac{h^2}{2I}J(J+1)$ $\Rightarrow \frac{6h^2}{I} = \frac{h^2}{2I}J(J+1)$ $\Rightarrow 12 = J(J+1)$

$(J = 3)$

$g_J = (2J+1) = 2\times 3+1$ $\Rightarrow \boxed{g_J = 7}$ degeneracy.

$E = \frac{10h^2}{\mu r^2}$ $\Rightarrow E = \frac{h^2}{2I}J(J+1)$

Put the value of E, $\frac{10h^2}{\mu r^2} = \frac{h^2}{2\mu r^2}J(J+1)$ $\Rightarrow 20 = J(J+1)$

10. The rotational constant B for CO is $1.932\times 10\ m^{-1}$. What is the J value corresponding to maximum relative population at 298K.

$J_{max} = ?$

Soln. $J_{max} = \frac{\sqrt{\frac{2kT}{B}} - 1}{2} = \sqrt{\frac{2kT}{2Bhc}} - \frac{1}{2} = \sqrt{\frac{1.38\times 10^{-23}\ \frac{J}{k-mole}\times 298}{2\times 1.932\times 10^{2}\times 6.6\times 10^{-34}\ J-sec\times 3\times 10^{8}\ m/sec}}$

$$= \sqrt{\frac{411.24\times 10^{24}\times 10^{-23}}{76.50}} - 0.5 = \sqrt{5.37\times 10^{1}} - 0.5 = \sqrt{53.7} - 0.5$$

$$\boxed{J_{max} = 6.81 \approx 7}$$

CLASSIFY MOLECULES :

Molecule	Top	Microwave activity
BF_3	Symmetric	inactive
BrF_3	Assymmetric	active
CO_2	linear	inactive
O_3	Assymmetric	active
SO_2	"	"
Cl_2	Linear	inactive
H_2O	Assymetric	active
$CH_2 = CH_2$	Symmetric	inactive
$CH \equiv CH$	linear	inactive
CO_3	linear	active
NH_3	symmetric	active
CH_3Cl	symmetric	active
HCN	linear	active
SF_6	Spherical	inactive
CH_2Cl	Assymmetric	active
CH_4	Spherical	inactive
$CH_2 = CHCl$	Assymmetric	active
HOCl	Assymmetric	active

11. The H–Cl molecule in the gaseous state shows pure rotational lines at the following frequency (in cm^{-1}) 20.7, 41.5, 62.0, 83.0 and 103.8. Assign these lines to the rotational transitions J→J+1. From the observed spectrum calculate the bond distance of HCl.

$J = 0 \rightarrow J = 1$	$20.7\ cm^{-1}$	
$J = 1 \rightarrow J = 2$	$41.5\ cm^{-1}$	$\Delta J = 41.5 - 20.7 = 20.8\ cm^{-1}$
$J = 2 \rightarrow J = 3$	$62.0\ cm^{-1}$	$\Delta J = 62.0 - 41.5 = 20.5\ cm^{-1}$
$J = 3 \rightarrow J = 4$	$83.0\ cm^{-1}$	$\Delta J = 83.0 - 62.0 = 21.0\ cm^{-1}$
$J = 4 \rightarrow J = 5$	$103.8\ cm^{-1}$	$\Delta J = 103.8 - 83.0 = 20.8\ cm^{-1}$

$$\text{Average spacing} = \frac{83.1}{4} = 20.77\ cm^{-1}$$

i.e. $2B = 20.77$; $B = \frac{20.77}{2}$; $B = 10.38\ cm^{-1}$

We know that,

$$I = \frac{h}{8\pi^2 BC}; \quad I = \frac{6.624 \times 10^{-34}\ J-s}{8 \times (3.14)^2 \times 10.38\ cm^{-1} \times 3 \times 10^{10}\ cm/s}$$

$$I = \frac{6.624 \times 10^{-44}}{8 \times (3.14)^2 \times 3 \times 10.38}\ Js^2; \quad I = \frac{6.624}{2457.88} \times 10^{-44}\ Js^2$$

$$I = \frac{6624 \times 10^{-47}}{2457.88}\ Js^2; \quad I = 2.695 \times 10^{-47}\ Js^2$$

Since $1\,J = 1\,kgm^2s^{-2}$

So, $I = 2.695\times10^{-47}\,kg\,m^2s^{-2}$; $I = 2.695\times10^{-47}\,kg\,m^2s^{-2}-s^2$.

Since, $\mu_{HCl} = \dfrac{35.5\times1}{35.5+1}\,amu$; $\mu_{HCl} = \dfrac{35.5}{36.5}\,amu$; $\mu_{HCl} = 0.772\,amu$

Since, $1\,amu = 1.67\times10^{-27}\,kg$

$\mu_{HCl} = 0.972\times1.67\times10^{-27}\,kg$

$\mu_{HCl} = 1.624\times10^{-27}\,kg$

We know that

$I = \mu r^2$

$\therefore \quad r^2 = \dfrac{I}{\mu}$ Or, $r = \sqrt{\dfrac{I}{\mu}}$

i.e. $r = \sqrt{\dfrac{2.695\times10^{47}\,kgm^2}{1.624\times10^{-27}\,kg}}$

$r = 12.9\times10^{-11}\,m$

$r = 1.29\,\text{Å}$ Ans.

12. What are the degeneracies of the following diatomic rotational energy level?

(a) 0 (b) $\dfrac{h^2}{I}$ (c) $\dfrac{6h^2}{I}$

Soln. Each energy level has (2J+1) fold degeneracies

$\therefore$ degeneracy = (2J+1) $E_J = \dfrac{h^2}{8\pi^2 I}J(J+1)$

Or, $E_J = \dfrac{h^2}{2I}J(J+1)$

(a) $E_J = 0$

degeneracy = $2J+1 = 2\times0+1 = 1$ (non degenerate)

(b) $E_J = \dfrac{h^2}{I}$; $\dfrac{h^2}{2I}J(J+1) = \dfrac{h^2}{I}$; $\dfrac{J(J+1)}{2} = 1$

Or, $J(J+1) = 2$

Or, $J^2 + J = 2$

Or, $J^2 + J - 2 = 0$

Or, $J^2 + 2J - J - 2 = 0$

Or, $J(J+2) - 1(J+2) = 0$

Or, $(J-1)(J+2) = 0$

i.e. $J-1=0$ Or, $J=1$

$J+2=0$ $J=-2$

degeneracy $=(2J+1)$

$=2\times1+1=3$

(c) $E_J=\frac{6\hbar^2}{I}$; $\frac{\hbar^2}{2I}J(J+1)=\frac{6\hbar^2}{I}$; $J(J+1)=12$

Or, $J^2+J-12=0$

Or, $J^2+4J-3J-12=0$

Or, $J(J+4)-3(J+4)=0$

Or, $(J-3)(J+4)=0$

Or, $(J-3)=0$ & $J+4=0$

$\therefore$ $J=3$

Therefore, degeneracy $=2J+1=2\times3+1=7$

13. The internuclear distance (i.e. bond length) of CO molecule is 1.13 Å. Calculate the energy in (Joules and ineV) and angular velocity of this molecules in the first excited rotational level. The atomic masses are.

$^{12}C=1.99\times10^{-26}\ kg$; $^{16}O=2.66\times10^{-26}\ kg$

Soln. $r=1.13\text{Å}=1.13\times10^{-8}\ cm=1.13\times10^{-10}\ m$

$$\mu=\frac{m_1m_2}{m_1+m_2}=\frac{\left(1.99\times10^{-26}\ kg\right)}{1.99\times10^{-26}kg+2.66\times10^{-26}kg}=\frac{1.99\times2.66\times10^{-52}\ kg^2}{(1.99+2.66)\times10^{-26}\ kg}$$

$$=\frac{5.2934}{4.65}\times10^{-26}\ kg$$

So, $\mu=1.138\times10^{-26}\ kg$ Or, $\mu=1.14\times10^{-26}\ kg$

Hence, the moment of intertia

$I=\mu r^2$; $I=1.14\times10^{-26}\ kg\times\left(1.13\times10^{-10}\right)^2$

$I=1.14\times1.13\times1.13\times10^{-46}\ kgm^2$; $I=1.455\times10^{-46}\ kgm^2$

i.e. $I=1.46\times10^{-46}\ kgm^2$

The rotational energy level of a rigid diatomic molecule are given by

$$E_J=\frac{h^2}{8\pi^2I}J(J+1)\ Joule$$

For the first excited rotational level, J = 1

Hence,

$$E_1=\frac{h^2\times1(1+1)}{8\pi^2I};\quad E_1=\frac{2h^2}{8\pi^2I}\qquad \text{i.e. } E_1=\frac{h^2}{4\pi^2I}J$$

Or, $$E_1=\frac{\left(6.626\times10^{-34}\ JS\right)^2}{4\times(3.14)^2\times1.46\times10^{-46}kgm^2}$$

$$E_1 = \frac{6.626\times6.626\times10^{-68}\ J^2.S^2}{4.314\times3.14\times1.46\times10^{-46}\ kgm^2}$$

$$E_1 = \frac{6.626\times6.626\times10^{-22}}{4\times3.14\times3.14\times1.46}\ J^2.S^2\ kg^{-1}m^{-2}$$

$$E_1 = \frac{43.90}{57.58}\times10^{-22}\ J^2S^2kg^{-1}\ m^{-2}$$

Or, $E_1 = 0.762\times10^{-22}\ J.J\ kg^{-1}m^{-2}s^2$ $\quad\therefore\quad E_1 = 7.62\times10^{-23}$

Since $1J = 1\ kgm^2S^{-2}$

Now, substituting these value, $E_1 = 7.62\times10^{-23}\ J$

Since, $1eV = 1.602\times10^{-19}\ J$ $\quad\therefore\quad E_1 = \frac{7.62\times10^{-23}}{1.602\times10^{-19}}eV$

$$\boxed{E_1 = 4.75\times10^{-4}\ eV}$$

Now, we know that

$E_1 = \frac{1}{2}I\omega^2$ Or, $I\omega^2 = 2E_1$ Or, $\omega^2 = \frac{2E_1}{I}$

$\therefore\quad \omega^2 = \sqrt{\frac{2E_1}{I}}$ i.e. $\omega = \sqrt{\frac{2\times7.61\times10^{-23}\ J}{1.46\times10^{-46}\ kgm^2}}$

Or, $\omega = \sqrt{\frac{15.22\times10^{23}}{1.46}}\ Jkg^{-1}m^{-2}$

Or, $\omega = \sqrt{10.42\times10^{23}}$

$\omega = 3.23\times10^{11}$ radian s^{-1}

14. The wave number of pure rotational lines of HBr are represented by the equation $\bar{\nu}_f = 16.90\ cm^{-1}$, where J has integral values. Calculate
(a) The moment of inertia
(b) The internuclear distance of HBr
(c) Rotational frequency and the period of rotation for the rotational quantum number 1.
(d) Which rotational energy level has the highest population at 298 K
(e) What is the change in rotational constant when H is replaced by D?

Soln. Since $2B = 16.90\ cm^{-1}$

$\therefore\quad B = \frac{16.90}{2} = 8.45\ cm^{-1}$

Or, $B = 8.45\ cm^{-1} = 8.45\times10^2\ m^{-1}$

(a) We know that, $B = \frac{h}{8\pi^2IC}$

$\therefore\quad I = \frac{h}{8\pi^2BC}$

Or, $I = \dfrac{6.624\times10^{-34}\ JS}{8(3.14)^2\times8.45\times10^2\ m^{-1}\times3\times10^8\ m/s}$; $I = \dfrac{6.624\times10^{-44}}{8\times(3.14)^2\times8.45\times3}\ Js^2$

Or, $I = \dfrac{6.624\times10^{-44}}{1999.52}\ J.S^2$; $I = \dfrac{6624}{1999.52}\times10^{-47}\ J.S^2$; $I = 3.3127\times10^{-47}\ JS^2$

Since $1\ J = kgm^2s^{-2}$

So, $U = 3.313\times10^{-47}\ kgm^2$ Ans.

(b) We know that $I = \mu r^2$

$\therefore$ $r = \left(\dfrac{I}{\mu}\right)^{1/2}$; $\mu = \dfrac{m_1m_2}{m_1+m_2} = \dfrac{1\times79}{1+79}\ amu$

Or, $\mu = \dfrac{79}{80}\ amu$ $\Rightarrow \mu = 0.98\ amu$

Or, $\mu = 0.98\times1.66\times10^{-27}\ kg$ $\Rightarrow \mu = 1.64\times10^{-27}\ kg$

Now, $r = \left(\dfrac{1}{\mu}\right)^{1/2}$ i.e. $r = \left(\dfrac{3.31\times10^{-47}\ kgm^2}{1.64\times10^{-27}\ kg}\right)^{1/2}$

Or, $r = \left(\dfrac{3.31}{1.64}\times10^{-20}\ m^2\right)^{1/2}$

Or, $r = \left(2.0182\times10^{-20}\ m^2\right)^{1/2}$

Or, $r = 1.42\times10^{-10}\ m = 1.42\times10^{-8}\ cm = 142\ pm$

(c) From classical mechanics, the kinetic energy E_k of the molecule is given by $E_k = \dfrac{1}{2}I\omega^2$

Or, $\omega^2 = \dfrac{2E_k}{I}$ $\Rightarrow \omega = \left(\dfrac{2E_k}{I}\right)^{1/2}$

Since $\Delta E = h\nu = h\times\dfrac{c}{\lambda} = hc\bar{\nu}$

$= 6.626\times10^{-34}\ JS\times3\times10^8\ m/s\times16.90\times10^2\ m^{-1} = 6.626\times3\times16.90\times10^{-24}\ J$

$= 335.938\times10^{-24}\ J$

$E_k = 3.35\times10^{-22}\ J$

Now, $\omega = \left(\dfrac{2\times3.35\times10^{-22}}{3.313\times10^{-47}\ kgm^2}\right)^{1/2}$

Or, $\omega = \left(\dfrac{2\times3.35}{3.313}\times10^{25}\ Jkg^{-1}m^{-2}\right)^{1/2}$ $\Rightarrow \omega = \left(\dfrac{6.70}{3\ 313}\times10^{25}\ J\ kg^{-1}m^{-2}\right)^{1/2}$

Or, $\omega = \left(2.02\times10^{25}\ J\ kg^{-1}m^{-2}\right)^{1/2}$ $\Rightarrow \omega = \left(20.20\times10^{24}\ J\ kg^{-\frac{1}{2}}m^{-2}\right)^{1/2}$

Or, $\omega = 4.50\times10^{12}\ J^{1/2}kg^{-1/2}m^{-1}$

Since, $1\ J = kgm^2s^{-2}$

So, $\omega = 4.50\times10^{12}\ s^{-1}$

$\omega = 4.50\times10^{12}s^{-1}$

Now, $\omega = 2\pi\nu$

Where ν is the frqeuency of rotation. Hence,

$$\nu = \frac{\omega}{2\pi} \quad \Rightarrow \nu = \frac{4.50\times10^{12}s^{-1}}{2\times3.14}$$

Or, $$\nu = \frac{4.50\times10^{12}}{6.28}s^{-1}$$

Or, $\nu = 0.716\times10^{12}s^{-1}$

Thus, period of rotation $\tau = \frac{1}{\nu}$ $\Rightarrow \tau = \frac{1}{7.16\times10^{11}}s^{-1}$

Or, $\tau = 1.395\times10^{-12}\ s$

(d) We know that, $I_{max} = \frac{1}{2}\left[\left(\frac{2kT}{Bhc}\right)^{1/2} - 1\right]$

Or, $$I_{max} = \frac{1}{2}\left[\left(\frac{2\times1.38\times10^{-23}\ JK^{-1}\times298K}{8.45\times10^{2}\ m^{-1}\times6.624\times10^{-34}\ J.S\times3\times10^{8}\ m/s}\right)^{1/2} - 1\right]$$

Or, $$= \frac{1}{2}\left[\left(\frac{2\times1.38\times298\times10^{-23}}{8.45\times6.624\times3\times10^{-24}}\right)^{1/2} - 1\right] = \frac{1}{2}\left[\left(\frac{2\times1.38\times298\times10}{8.45\times6.624\times3}\right)^{1/2} - 1\right]$$

Or, $$= \frac{1}{2}\left[\left(\frac{8224.8}{167.918}\right)^{1/2} - 1\right] = \frac{1}{2}\left[(48.98)^{1/2} - 1\right] = \frac{1}{2}[6.80 - 1] = \frac{1}{2}\times5.80 = 2.9$$

Or, $I_{max} = 2.9 \approx 3$

(e) The substitution of H by D does not affect the internuclear distance of HBr but changes only its reduced mass. Since B is inversely related to 'I' we may write

$$\mu_{DBr} = \frac{m_D m_{Br}}{m_D + m_{Br}} \quad \Rightarrow \mu_{DBr} = \frac{2\times79}{2+79}amu$$

Or, $$\mu_{DBr} = \frac{158}{81}amu \quad \Rightarrow \mu_{DBr} = 1.95\ amu$$

i.e. $\mu_{DBr} = 1.95\times1.66\times10^{-27}\ kg$ $\Rightarrow \mu_{DBr} = 3.23\times10^{-27}\ kg$

Since, $\frac{B_{DBr}}{B_{HBr}} = \frac{\mu_{HBr}}{\mu_{DBr}}$ $\therefore$ $B_{DBr} = \frac{\mu_{HBr} \times B_{HBr}}{\mu_{DBr}}$

Or, $B_{DBr} = \left(\frac{1.64\times10^{-27}\,kg}{3.23\times10^{-27}\,kg}\right)\times 8.45\,cm^{-1} \Rightarrow B_{DBr} = \left(\frac{1.64}{3.23}\times 8.45\,cm^{-1}\right)$

Or, $B_{DBr} = 0.507\times 8.45\,cm^{-1}$

Or, $B_{DBr} = 4.29\,cm^{-1}$

15. The first rotational line for CO appears at 3.84 Cm^{-1} where will be the position of third rotation line?

Soln. First 2B ⟶ 3.84 — Ist line = 2B

1B ⟶ $\frac{3.84}{2}$ — IInd Line = 4B

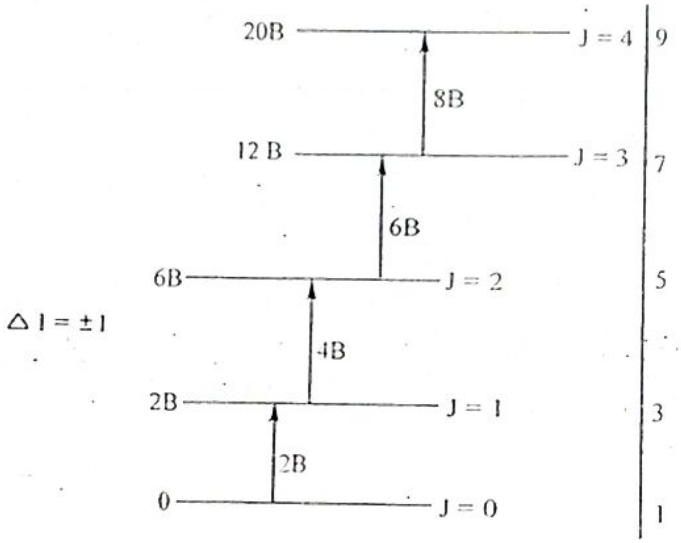
IIIrd Line = 6B

6B ⟶ $\frac{3.84\times 6}{2} = 11.52$

Third line at 11.52 Cm^{-1}.

INTENSITY OF SPECTRAL LINES:

Intensity of lines are directly proportional to the initial no. of moleculesin each energy levels.



The population is governed by the 2 factors.

(1) Boltzmann's distribution Constant – According to which population decreasing by increasing the energy of the levels.

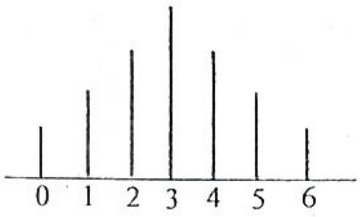
$$\frac{N_{J+1}}{Ni} = \exp-\left[\frac{-Bhc\,J(J+1)}{KT}\right]$$

(2) Degeneracy of each energy level i.e. = 2(J+1) and population increases are the degeneracy increases. Hence relative population comes from the effect of both factors and is directly

$$\alpha\,(2J+1).\exp\left(-\frac{\sum_J}{KT}\right)$$

Maximum population comes at $\boxed{J = \sqrt{\frac{KT}{2hcB}} - \frac{1}{2}}$

Hence the intensities of rotational lines will be very low at very less J value as well as very high J value.



ISOTOPIC SUBSTITUTION :

Effect of

* Isotopic Substitution :

Effect on the rotational spectrum :

$B = \frac{h}{8\pi^2 Ic}$ $\quad I = \mu r_0^2$

$\mu = \frac{m_1 m_2}{m_1 m_2}$

$^{1}H—^{35}Cl$ $\quad$ $^{1}H—^{37}Cl$

$\therefore$ Energy levels $E_J = BJ(J+1)$

(1) On isotopic substitution there will be no change in the bond length.

- Substitution of lighter isotop by heavier isotope.
- Substitution of lighter isotope.
- Substitution by heavier isotope.
  - μ will increase
  - I will increase
  - B will decrease
  - Seperation between rotational energy level will reduce/decrease.
  - Spectral line will become closer.

Substitution by lighter isotope $\rightarrow \mu$ will decrease
Substitution of heavier isotope $\rightarrow$ I will decrease
$\rightarrow \beta$ will increase

- Separation of energy level increase
- Spectral line becomes far apart

By the use of isotopic substitution we can find out precise atomic wt. and bond lengths of isotope substituted molecules.

$C \equiv O^{16}$	$C \equiv O^{18}$	
μ	μ'	$\mu < \mu'$
I	I'	I < I'
β	β'	$\beta > \beta'$
r_0	r_0	$r_0 = r_0$

$\beta = \frac{h}{8\pi^2 Ic}$ $\quad \boxed{\frac{\beta}{\beta'} = \frac{I'}{I} = \frac{\mu'}{\mu}}$

NON RIGID ROTATOR :

$$\boxed{\epsilon_J = BJ(J+1)\,cm^{-1}}$$

$$\beta \alpha \frac{1}{I} \alpha \frac{1}{r} \alpha \frac{1}{r_0^2}$$

Rigid rotator spectrum	Rigid rotator	non rigid rotator
20B	———	J = 4
12B	———	J = 3
6B	———	J = 2
2B	———	J = 1
0	———	J = 0

Assumption of rigid bond is only approrimation but in reality all the bond are elastic some extent. When molecule rotates then due to centripetal force the bond length increases and since

$$\beta \alpha \frac{1}{r_0^2}$$

The value of rotational constant decreases. Hence in the higher rotational energy levels the speed of rotation incresase and value of B will decrease. So these higher energy levels some what closer than the rigid rotator.

Rigid	Non - Rigid
(1) The value of B form any spectral line of rigid rotator will be same	(1) The value of B will decrease continuously in higher spectral lines.
(2) Rotational energy levels will be some what far apart than non-rigid rotator.	(2) Rotational energy levels will be more closer in non-rigid rotator than that of rigid rotator.
(3) The spectral line will be some what far apart from each other than non rigid rotator	(3) The spectral line will be some what closer from one another than rigid rotator.

In the lower energy levels the non-rigid rotator behaves similar to the rigid rotator hence we calculate the bond length we should obtain the value of rotational constant from initial spectral lines.

Since the bond length changes according to simple harmonic motion applying the rules of SHM on schrodinger wave equation the formula of energy level.

$$E_J = BJ(J+1) - DJ^2(J+1)^2 + HJ^3(J+1)^3 + KJ^4(J+1)^4 \ldots\ldots$$

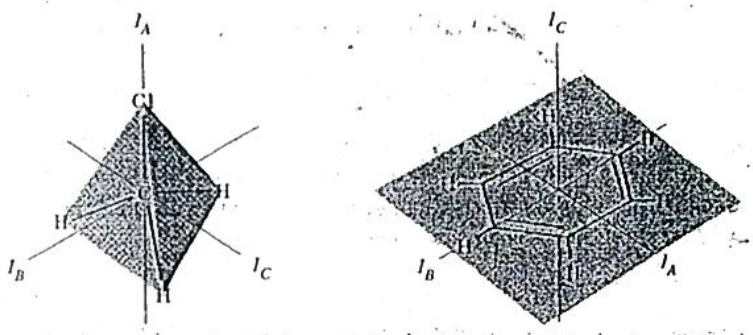
Where D,H,K are centrifugal distortion constant. Their values decreases as D>H>K). Hence only the value of D affect the spectrum the effect of H.K & higher constants will be negligible. So it equation can be summerised as

$$\boxed{E_J = BJ(J+1) - DJ^2(J+1)^2}$$

The value of $\boxed{D = \frac{h^3}{32\pi^4 I^2 r^2 k\, c}\, cm^{-1}}$ $\Rightarrow \boxed{D = \frac{4B^3}{\bar{\omega}^2}}$

Here $\bar{\omega}$ is vibrational frequency.

SYMMETRIC TOP MOLECULES :



Prolate symmetric top
$I_A < I_B = I_C$
(a)

Oblate symmetric top
$I_C > I_A = I_B$
(b)

The energy level of a **oblate symmetric top** are given by

$$\epsilon_{J,k} = BJ(J+1) + (C-B)K^2 \ \ cm^{-1}$$

With J = 0, 1, 2, ... and K = K = 0, ± 1, ± 2, ..., ±J

The energy level of a **prolate symmetric top** are given by

$$\epsilon_{J,k} = BJ(J+1) + (A-B)K^2 \ \ cm^{-1}$$

Selection rule $\Delta J = \pm 1 \ \ \Delta K = 0$ for K=0
$\Delta J = 0, \pm 1 \ \ \Delta K = 0$ for $K \neq 0$

Hence the energy levels on the z-axis for which rotational quantum no. K are inactive to give spectrum.

J ——— (J + 1)

$\epsilon_J \rightarrow \epsilon_{J+1} = 2B(J+1) cm^{-1}$ same as linear molecule.

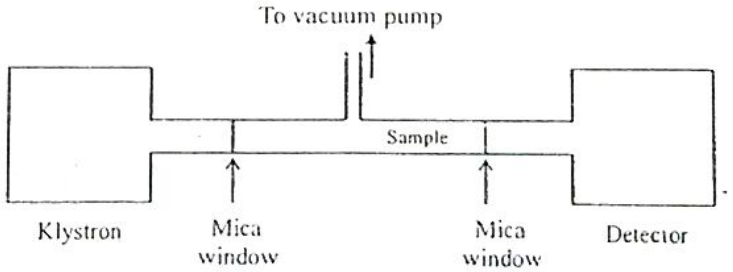
INSTRUMENTATION :

(1) Source (2) Sample (3) detector

Source - Klystron value - it gives monochromatic microwave rotation
(radiation of one frequancy)

Sample and sample space- Normally the sample is gaseous and is retained in a piece of evacuated waveguide by very thin mica windows. Very small pressures are sufficient to obtain a spectrum.

Detector : Radio recover crystal detector.



SOLVED PROBLEMS

1. The microwave spectrum of a molecule yields three rotational constants. The molecule is
(a) Prolate symmetric top (b) Spherical top **[NET-June 2011]**
(c) Asymmetric top (d) Oblate symmetric top

Soln. For an asymmetric top, $I_x \neq I_y \neq I_z$

$\therefore$ Total energy $(E) = E_x + E_y + E_z$

$$= \frac{J_x^2}{2I_x} + \frac{J_y^2}{2I_y} + \frac{J_y^2}{2I_z}$$

So, above equation will give three rotational constants, B_x, B_y & B_z.

Correct answer: (c)

2. For a diatomic molecule AB, the energy for the rotational transition from J = 0 to J = 1 state is 3.9 cm^{-1}. The energy for the rotational transition from J = 3 to J = 4 state would be **[NET-June 2012]**
(a) 3.9 cm^{-1} ———(b) 7.8 cm^{-1} (c) 11.7 cm^{-1} (d) 15.6 cm^{-1}

Soln. J = 0 to J = 1 appears at 2B = 3.9 cm–1.
Value of rotational constant B = 3.9/2 = 1.95

$$\Delta E = \Sigma_{J_1} - \Sigma_{J_1} = 20B - 12B = 8B = \frac{3.9}{2} \times 8 = 3.9 \times 4 = 15.6 \text{ cm}^{-1}$$

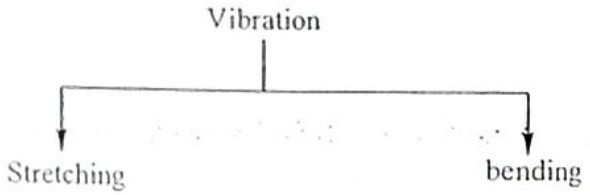
Correct answer is (d).

IR SPECTROSCOPY

Range : 400 _____ 4000 cm^{-1}

VIBRATIONAL MOTION :

Structural information from vibrational motion of molecule. Every molecule posses a vibrational frequency means bond behaves as spring H〰〰〰(Cl) vibration are simple Harmonic motion (SHM)



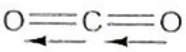
IR ACTIVE MOLECULE : For a molecule to be IR active there should be change in the dipole moment in its vibrational motion.

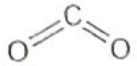
For a vibration to be IR active there should be change in the dipole moment in the molecule i.e. if there is no change in the dipole moment on vibration that vibration will be IR inactive.

Activity of molecule Activity of vibration.

O=C=O molecule IR active

(1) Symmetric strech no change in dipole moment, So I.R. inactive

(2) Assymmetric strech  change dipole, IR active

(3) Bend  change in dipole, IR active

When the frequency of this fluctuating dipole becomes equal to the IR radiation absorption takes place to give IR spectrum. If we apply SHM on a vibrating bond then its frequency $\bar{\omega}$

$$\bar{\omega} = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}}\ Hz \qquad \mu = \frac{m_1 m_2 - - -}{m_1 + m_2}$$

K = force constant

C ≡ O $\upsilon C-C > \upsilon C-O > \upsilon C-Cl$

(i) Frequency position of signal

(ii) Intensity High of signal

Frequency of vibration depend on the force constant K and reduced mass μ. The force constant of all single bond are almost same, all double bond almost same & all triple bonds almost same. It means if we compare. The frequency of different singal bonds then we can use reduce mass.

Intensity depend on change in the value of dipole moment on vibration magnituds of change i.e. higher the magnitude higher will be intensity.

Example: C–F C–Cl

$\upsilon_{C-F} > \upsilon_{C-Cl}$

$\upsilon_{c-F} > \upsilon_{C-Cl}$

Hence the intensity of vibration of more polar bond will be more.

SOLVED PROBLEMS

1. Which will be IR frequency > P = 0 > C = 0

Soln: $\upsilon > P = 0 \quad < \upsilon > C = 0$

$$\begin{cases} \text{frequency} \rightarrow \text{polarity} \\ \text{intensity} \rightarrow \text{reduced mass} \end{cases}$$

2. Arrange the following bond in increase vibrational frequency

C—O , C—N , C—H , H—H

Soln. $\upsilon_{H-H} > \upsilon_{C-H} > \upsilon_{O-H} > \upsilon_{C-N} > \upsilon_{C-O}$

$\equiv C^{sp}—H$

$= C^{sp^2}—H$

$—C^{sp^3}—H$

If we consider only the rules of SHM for I.R. spectrum then IR. spectrum of these C–H bond should be same but in reality is different hence only force constant and reduced mass μ are not the parameters for IR frequencies but electronic factors are also important.

3. Classify the following molecules as I.R. active and microwave active

	IR active	**microwave active**
H_2	inactive	inactive
HCl	active	active
BF_3	active	inactive
CH_4	active	inactive
H_2O	active	active
Trans N_2H_2	active	inactive

By the application of principle of SHM on schrodinger wave equation we get the quantum mechanical explanation for vibrational motion.

Energy level diagram:

Since, $v = 1$ $\quad E_0 = \frac{1}{2}hv$

$x = 1$ $\quad E_1 = \frac{3}{2}hv$

$x = 2$ $\quad E_2 = \frac{5}{2}hv$

Conclusion:

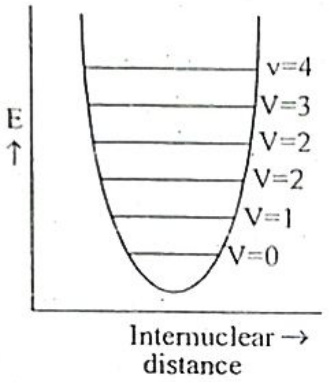
(i) The energy levels are equally spaced, i.e. the difference between the two nearest levels is the same throughout and has a value of $h\bar{v}\ cm^{-1}$.

(ii) The lowest vibration energy $(v = 0)$ is not zero as in the case of classical vibration but has a value of $\frac{1}{2}h\bar{v}$.

Since, $E_v = \left(v + \frac{1}{2}\right)\bar{v}\ cm^{-1}$; $v = 0$

So, $E_v = \left(0 + \frac{1}{2}\right)\bar{v}\ cm^{-1}$ i.e. $E_v = \frac{1}{2}\bar{v}\ cm^{-1}$

Schematic repr ented by energy level:



Vibrational energy levels for a diatomic molecule undergoing SHM.

The lowest energy is known at zero point energy (ZEP). This means that the atoms in a molecule can never be completely at rest relative to each other.

In classical mechanics the minimum vibrational energy which a diatomic molecule can posses is zero, i.e. the atoms can be at rest relative to each other.

The zeropoint energy is just half of the energy difference between the two nearest vibrational energy levels. It may be noted that both these quantities depend on the classical vibration frequency and hence on the strength of the chemical bond and the atomic masses.

Resonance condition:

$$E_{v+1} \rightarrow \nu = \left(v+\frac{1}{2}+1\right)\bar{\nu} - \left(v+\frac{1}{2}\right)\bar{\nu} \qquad \Rightarrow E_{v+1} \rightarrow \nu = \left(v+\frac{3}{2}\right)\bar{\nu} - \left(v+\frac{1}{2}\right)\bar{\nu}$$

$$\Rightarrow \quad E_{v+1} \rightarrow \nu = v\bar{\nu} + \frac{3}{2}\bar{\nu} - v\bar{\nu} - \frac{1}{2}\bar{\nu} \qquad \Rightarrow E_{v+1} \rightarrow \nu = \frac{3}{2}\bar{\nu} - \frac{1}{2}\bar{\nu}$$

Or, $\quad E_{v+1} \rightarrow \nu = \bar{\nu}\ cm^{-1}$

Harmonic Oscillator
(ideal)

Anharmonic Oscillator
(Real)

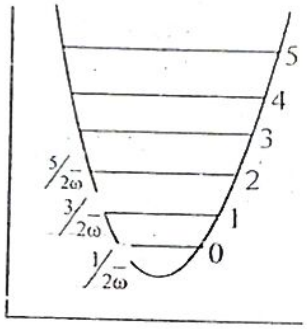
e.g. :

HARMONIC OSCILLATOR : A harmonic oscillator is approximation for all the bonds for harmonic oscillator a plot of internuclear distance against energy of the system is always parabola and the oscillation frequency of this oscillator can be given by

$$\bar{\omega}_{osc} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}\ cm^{-1}$$

By application of this formula the schrondinger wave equation we get formula of vibration energy level of harmonic oscillator.

$$\boxed{\epsilon_v = \left(\upsilon+\frac{1}{2}\right)\bar{\omega}_{osc}\ cm^{-1}}$$



$\frac{5}{2}\bar{\omega}_{osc}$ ——— $\upsilon = 2$

$\frac{3}{2}\bar{\omega}_{osc}$ ——— $\upsilon = 1$

$\frac{1}{2}\bar{\omega}_{osc}$ ——— $\upsilon = 0$

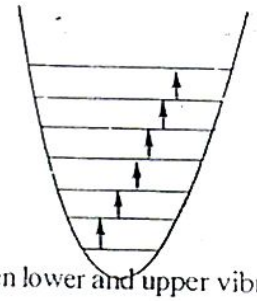
Hence vibrational energy level of simple harmonic oscillator are equally spaced. The energy related to the vibrational quantum number 0 is $\frac{1}{2}\bar{\omega}_{osc}$, and known as zero point energy.

zero point energy is basic difference between classical & quantum mechanics of vibrational motion. According to quantum mechanics molecule must always vibrate to some extent event at 0°K.

$$\epsilon_v = \left(\upsilon+\frac{1}{2}\right)\bar{\omega}_{osc}$$

Selection rule $\Rightarrow \qquad v = \pm 1$

$$\boxed{\sum \upsilon + 1 - \sum \upsilon = \bar{\omega}_{osc}\ \ cm^{-1}}$$



• The transition moment of a transition between lower and upper vibrational state with vibrational function, ψ'_v & ψ''_v is given by

$$\boxed{R_v = \int \psi'_v\, \mu \psi''_v\, d\tau} \qquad \boxed{I = \int \left(\psi'_v\, \mu \psi''_v\right)^2}$$

Where, R_v = transtion moment in the form dipole moment

I = Intensity in the form of dipole moment.

μ = dipole moment

$d\tau = dx$

x is the displacement of internuclear distance from the equilibrium

$$\boxed{x = r - \mu_e}$$

The dipole moment $\mu = 0$ for a Homo nuclear diatomic molecule that results transition moment $v = 0$ and all vibrational transition is forbidden.

- For internuclear diatomic molecule $\mu \neq 0$ and the varies with X.

  The variation can be expressed by Taylor Series.

$$\mu = \mu_e + \left(\frac{d\mu}{dx}\right)_e x + \left(\frac{d\mu}{dx}\right)_e^2 x^2 + \ldots\ldots$$

'e' refers to equilibrium configuration. The transition moment.

$$\int \psi'_v \mu \psi''_v \, dx = \int \psi'_v \mu_e \psi''_v \, dx + \int \psi'_v \left(\frac{du}{dx}\right)_e x \psi''_v \, dx$$

μ_e : 0

- When $v' \neq v''$ than first term is zero

$$R = \int \psi'_v \mu \psi''_v \, dx \qquad \Delta v = \pm 1$$

$$R = \int \psi'_v \left(\frac{du}{dx}\right)_e x \psi''_v \, dx$$

$dv = \pm 1$ constitution the vibrational selection rule.

The first term in the series is zero only if ψ'_v and ψ''_v are orthogonal. The population factor may be calculated by Boltzmann distribution

i.e. $$\boxed{\frac{N_v}{N_0} = \frac{g_v}{g_0} e^{-(E_v - E_0)/kT}}$$

that may be derived from Boltzmann Distribution law,

$$\boxed{\frac{N_n}{N_m} = \frac{g_n}{g_m} e^{-(E_n - E_m)/kT}}$$

If n and m are will be same than same level are illustrated. If the degree of degeneracy g_n and g_m of state n and m are same.

If $g_n = g_m$ $$\boxed{\frac{N_n}{N_m} = e^{-\Delta E/kT}}$$

If $g_v = g_0$ $$\boxed{\frac{N_v}{N_0} = e^{-\Delta E/kT}}$$

The energy difference v' and v" is

$v' = v \qquad \Rightarrow v'' = v + 1$

$$E_n = \left(n + \frac{1}{2}\right)h\nu \qquad \Rightarrow E_{n+1} - E_n = \left(n + \frac{3}{2}\right)h\nu - \left(n + \frac{1}{2}\right)h\nu = h\nu$$

$$\boxed{E_{v+1} - E_v = h\nu}$$

v = vibrational quantum number.

- Molecule has an harmonic oscillator. The spacing between vibration levels are larger than the spacing between rotational level of molecule. Infact larger than kT at room temperature. Hence, most of the molecule in a sample exist in n = 0 state with only their zero point energy.
  But situation is different for rotational state majority of the molecule at room temperature exist in higher rotational state.
  Real molecule does not follow the rule of SHM and anharmonicity generates in the molecule. If the expression for the dipole moment and polarazibility where linera in X than μ and α could be harmonic. The effect of higher terms is k/as anharmonicity.
- Dipole moment is varies in X
- The Schrodinger wave equation and perturbation method was used to calculate the eigen value of energy of anharmonic oscillator and it was given by the equation

$$\boxed{E = \left(n + \frac{1}{2}\right) h\nu \;\; h\nu_e - \left(n + \frac{1}{2}\right)^2 h\nu_e x_e}$$

x_e = anharmonicity constant.

- Energy may be represented in the form of dissociation energy and morse potential.

$$\boxed{v = D_e\left[1 - e^{-ax}\right]^2}$$

a and D are constant.

$$\boxed{x = r - r_e}$$

It is k/as potential function related to the behaviour of anharmonic oscillator.

D_e = Dissociation energy

$$E = \left(n + \frac{1}{2}\right) h\nu - \left(n + \frac{1}{2}\right)^2 h\nu x_e$$

Wave number $= \left(n + \frac{1}{2}\right)\bar{\nu} - \left(n + \frac{1}{2}\right)^2 \bar{\nu}\, x_e \text{ cm}^{-1}$

$$\boxed{\bar{E}_n = \left(n + \frac{1}{2}\right)\bar{\omega}_e - \left(n + \frac{1}{2}\right)^2 \bar{\omega}_e x_e}$$ n and (n + 1) level

$$E_{n+1} - E_n = \left[\left(n + 1 + \frac{1}{2}\right)\omega_e - \left(n + 1 + \frac{1}{2}\right)^2 \omega_e x_e\right] - \left[\left(n + \frac{1}{2}\right)\omega_e - \left(n + \frac{1}{2}\right)^2 \omega_e x_e\right]$$

$$= \omega_e - \left(n + \frac{3}{2}\right)^2 \omega_e x_e + \left(n + \frac{1}{2}\right)^2 \omega_e x_e$$

$$\boxed{E_{n+1} - E_n = \omega_e - \left[\left(n + \frac{3}{2}\right)^2 - \left(n + \frac{1}{2}\right)^2\right]\omega_e x_e}$$

$$= \omega_e - \left[\left[n^2 + \frac{9}{4} + \frac{2.3}{2} n\right] - \left[n^2 + \frac{1}{4} + 2n\frac{1}{2}\right]\right]\omega_e x_e$$

$$= \omega_e - \left\{\frac{9}{4} + 3n - \frac{1}{4}n\right\}\omega_e x_e = \omega_e\left[2 + 2n\right]\omega_e x_e$$

$$\boxed{E_{n+1} - E_n = \omega_e - \left[1+n\right]2\omega_e x_e}$$

If $n = 0$, $\boxed{E_0 + 1 - E_0 = \omega_e - 2\omega_e x_e}$

If $n = 1$, $E_2 - E_1 = \omega_e - \left[1+1\right]2\omega_e x_e$; $\boxed{E_2 - E_1 = \omega_e - 4\omega_e x_e}$

If $n = 2$, $E_{2+1} - E_2 = \omega_e - (2+1)2\omega_e x_e$; $\boxed{E_3 - E_2 = \omega_e - 6\omega_e x_e}$

SOLVED PROBLEMS

1. The value of ω_e are 4395, 3817, 3118 cm^{-1} for H_2, HD and D_2 molecules respectively. The value of $\omega_e x_e = 118, 95, 64\ cm^{-1}$ for the same molecule. Calculate the zero point energy of the molecule in kcal/mol.

$\overline{v} = \omega_e = 4395\ (H_2)$ $\Rightarrow \overline{v} = \omega_e = 3817\ (HD)$ $\Rightarrow \overline{v} = \omega_e = 3118\ (D_2)$

$$E = \left(n + \frac{1}{2}\right)\overline{v} - \left(n + \frac{1}{2}\right)^2 \overline{v}x_e$$

For zero point energy $(n = 0)$

$$E_0 = \frac{1}{2}\overline{v} - \frac{1}{4}\overline{v}\, x_e$$

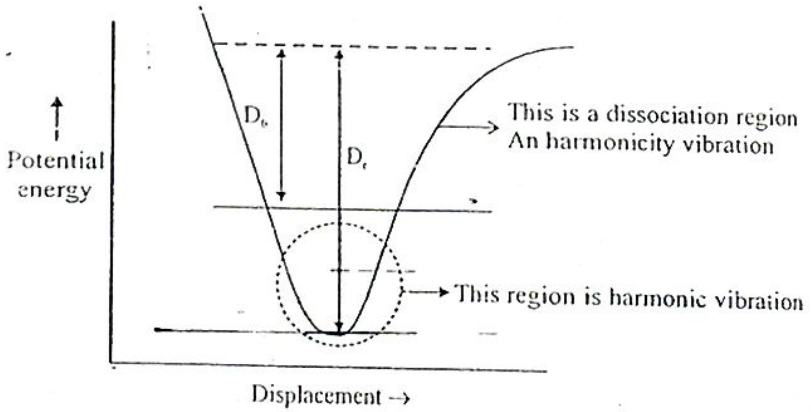
For H_2: $E_0 = \frac{1}{2}(4395) - \frac{1}{4} \times 118 = 2168\ cm^{-1} \times hc\ J$

Multiply by R and divide by R

$$= 2168\ cm^{-1} \times hc(J) \times \frac{2cal}{8.314J} = \frac{2168 \times 6.62 \times 10^{-34} \times 3 \times 10^8 \times 2\ cal}{8.314}$$

$$= \frac{85852.8 \times 10^{-26}}{8.314} = 10326.29g0^{-26} = 10.32 \times 10^{-23}$$

If we put a graph between potential and displacement



$$D_0 = D_e - \frac{1}{2}h\nu \qquad \Rightarrow D_0 = D_e - \frac{1}{2}\frac{h\nu}{hc}$$

$$D_0 = D_e - \frac{1}{2}\frac{\nu}{c} = D_e - \frac{1}{2}\bar{\nu} \qquad \boxed{D_0 = D_e - \frac{1}{2}\bar{\nu}}$$

$$E = \left(n+\frac{1}{2}\right)\bar{\nu} - \left(n+\frac{1}{2}\right)x_e\bar{\nu}$$

As we increase the level anharmonicity increase due to $\left(n+\frac{1}{2}\right)^2 x_e\bar{\nu}$ this term increase.

$$E = \left(n+\frac{1}{2}\right)\bar{\nu} - \left(n+\frac{1}{2}\right)^2 x_e\bar{\nu}$$

At higher level anharmonicity greater become last term.

- Schrodinger equation can be solved for the morse potential and permitted energy level is

$$E = \left(n+\frac{1}{2}\right)\bar{\nu} - \left(n+\frac{1}{2}\right)^2 x_e\bar{\nu}$$

x_e is anharmonicity constant $x_e = \dfrac{\bar{\nu}}{4D_e}$

The second term in the formula effect the system as 'n' increased and at high quantum number conversions of the level occur. Morse oscillation give a endless solution.

$$\boxed{E = \left(n+\frac{1}{2}\right)\bar{\nu} - \left(n+\frac{1}{2}\right)^2 x_e\bar{\nu} + \left(n+\frac{1}{2}\right)^3 y_e\bar{\nu} - \left(n+\frac{1}{2}\right)^n z_e\bar{\nu}}$$

But we focuse only first two terms. $x_e > y_e > z_e$

Anharmonicity also accounts for the appearance of additional weak absorption line corresponding to the transition $1 \rightarrow 2, 0 \rightarrow 3$ and so on. These are k/as overtone (I, II and III overtone)

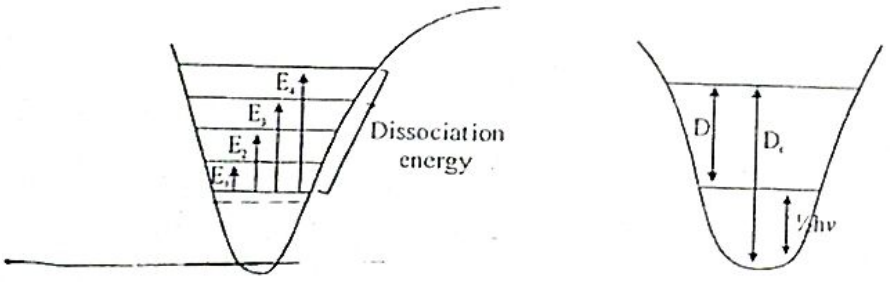
Overtones are forbidden

$\because$ $[\Delta v = \pm 1]$ $+1$ absorption

-1 emission

The reason for the appearance of overtone is selection rule is derived from the properties of harmonic oscillator wave function which are only approximately valid when anharmonicity is not.

Therefore, selection rule is also only an approximation.



$$\boxed{D = E_1 + E_2 + E_3 + E_4}$$

2. The first five vibrational level of HCl is 1481.06, 4367.50, 7149.04, 9826.48, 12399.8 cm^{-1}. Calculate the dissociation energy in cm^{-1}.

$\omega_e = ?$ $\omega_e x_e = ?$

Soln. $D_e = \dfrac{\bar{v}}{4x_e} \Rightarrow D_0 = D_e - \dfrac{1}{2}\bar{v}$

$\omega_e - 2\omega_e x_e = 1481.86 \times 3$ ....(1)

$3\omega_e - 12\omega_e x_e = 4367.50$ ....(2)

$3\omega_e - 6\omega_e x_e = 4420.44$

$-3\omega_e - 12\omega_e x_e = 4368.50$

$6\omega_e x_e = 52.99$

$\omega_e x_e = 8.823$

$\omega_e = 2 \times 8.823 = 1481.86$

$\omega_e = 1481.86 + 17.64$

$\omega_e = 1499.50$ $\qquad x_e = 0.0058$

$x_e = 5.8 \times 10^{-3}$

$$D_e = \frac{1499.50}{4 \times 5.8 \times 10^{-3}} = \frac{1499.50 \times 10^3}{23.2} = 64.63 \times 10^3$$

$$D_0 = D_e - \frac{1}{2}\bar{v} = 64.63 \times 10^3 - \frac{1}{2} \times 1499.50 = 64.6336 \times 10^3 - 749.75$$

$D_0 = 63883.85 = 63.883 \times 10^3$

3. Given that the spacing of line in microwave spectra of $^{35}Cl\,^{19}F$ is constant at 1.033 I, $\gamma = ?$

Soln. $2B = 1.033 \Rightarrow B = 0.5169$

$$\mu = \frac{35 \times 19}{35 + 19} \times 1.67 \times 10^{-27} = \frac{1110.55 \times 10^{-27}}{54} = 20.56 \times 10^{-27} \text{ kg/mol}$$

$$I = \frac{h}{8\pi^2 BC} = \frac{6.6 \times 10^{-34}}{8 \times (3.14)^2 \times 0.516 \times 3 \times 10^{10}} = \frac{6.6 \times 10^{-34} \times 10^{-10}}{122.21}$$

$I = 0.054 \times 10^{-44}$ $\qquad \Rightarrow I = \mu r^2$

$$r = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{0.054 \times 10^{-44}}{20.56 \times 10^{-27}}} = \sqrt{380.73 \times 10^{-17}} = \sqrt{38.0 \times 10^{-16}}$$

$$\boxed{r = 6.16 \times 10^{-8}}$$

4. The vibrational constant for O_2 molecule is 1580 cm^{-1}. Calculate the maximum displacement in $(r - r_e)$ in Å

$r_e = 1.207Å$

When $n = 0$, $n = 15$. Assuming that the molecule is harmonic oscillator and r_e is the equilibrium internuclear distance and find out % displacement.

$\Rightarrow$ ω_e = vibrational constant = 1580 cm^{-1}.

$\Rightarrow$ $r_e = 1.207Å = 1.207 \times 10^{-10}$ m

Potential energy at maximum displacement $x_e = r - r_e$

$$E = \left(n + \frac{1}{2}\right)h\nu - \left(n + \frac{1}{2}\right)^2 h\nu x_e$$

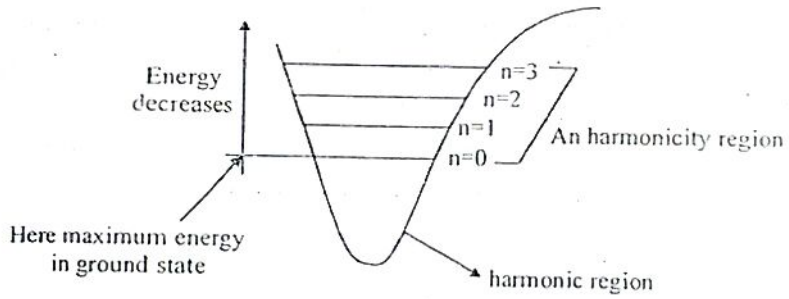
$$\boxed{x = \frac{r - r_e}{r_e} \times 100}$$

- The internuclear displacement $x_e = r - r_e$ may be expressed in the form of anharmonicity anharmonicity are of two type.

(1) Electrically anharmonicity
(2) Mechanically anharmonicity

5. Which type of anharmonicity depict the maximum displacement?

$$x_{ma} = \sqrt{\frac{h}{2J}}\left(\frac{1}{k\mu}\right)^{1/2}\sqrt{\left(V + \frac{1}{2}\right)}$$



$$k = 4\pi^2 c^2 \mu \omega_e^2 = 4 \times (3.14)^2 \times \left(3 \times 10^{10}\right)^2 \left(12.8 \times 10^{-27}\right)(1580)^2$$

$$= 1514.4 \times 10^{-7} \times 2496400 = 1514.4 \times 0.2496$$

$\therefore$ $k = 378.05$

$$x_{max} = \sqrt{\frac{6.634 \times 10^{-34}}{2 \times 3.14}}\left(\frac{1}{\sqrt{378.05 \times 12.8 \times 10^{-27}}}\right)^{1/2}\sqrt{\left(0 + \frac{1}{2}\right)} = \sqrt{1.050 \times 10^{-34}} = 1.02 \times 10^{-17}$$

$x_{max} = 0.05Å$ $\Rightarrow$ $\frac{x_{max}}{x_e} \times 100 = \frac{0.05}{1.207} \times 100$ $\boxed{\approx 4.14\%}$

ISOTOPIC EFFECT ON VIBRATIONAL LEVEL

The vibrational frequency, $\dot{\nu} = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}}$ for a harmonic oscillator the force constant 'k' is determine by electronic motion and is therefore, exactly the same for different isotopic molecule. The reduce mass is different for different isotop molecule.

If ν' is the vibrational frequency of isotope than

$$\frac{\nu}{\nu'} = \sqrt{\frac{\mu'}{\mu}}$$

k = same because it depend on electronic motion and the vibrational constant.

$$\frac{\omega_e}{\omega_e'} = \frac{\nu}{\nu'} = \sqrt{\frac{\mu'}{\mu}} = \rho$$

For heaviour isotopes

$\nu' < \nu \rightarrow$ smaller frequency.

$$\boxed{\nu = \rho\nu'}$$

ρ greater than 1

Heaviour isotopes have smaller freuqency because frequency is depend upon reduce mass.

$$\text{Frequency} \propto \frac{1}{\sqrt{\text{reduce mass}}}$$

Because reduce mass is high so frequency is low

$$\left[\text{H.I.} = \frac{127}{128} = \mu \quad \Rightarrow \text{DI} = \frac{254}{129} = \mu\right]$$

$$\boxed{\frac{\nu'}{\nu} = \sqrt{\frac{\mu}{\mu'}}} \quad \text{here,} \quad \boxed{\rho < 1}$$

If anharmonicity is taken into account than

$$\rho = \frac{\omega_e'}{\omega_e} = \frac{\nu'}{\nu} = \sqrt{\frac{\mu}{\mu'}} \qquad \Rightarrow E_V = \left(n+\frac{1}{2}\right)\omega_e - \left(n+\frac{1}{2}\right)^2 \omega_e x_e$$

For Isotope:

$$E_V' = \left(n+\frac{1}{2}\right)\omega_e' - \left(n+\frac{1}{2}\right)^2 \omega_e x_e$$

$$\left(\omega_e' = \rho\omega_e\right) = \left(n+\frac{1}{2}\right)\rho\omega_e - \left(n+\frac{1}{2}\right)^2 \rho\omega_e x_e$$

$$E_V' - E_V = (\rho-1)\left(n+\frac{1}{2}\right)\omega_e - (\rho-1)\left(n+\frac{1}{2}\right)^2 \omega_e x_e$$

$$= (\rho-1)\left[\left(n+\frac{1}{2}\right)\omega_e - \left(n+\frac{1}{2}\right)^2 \omega_e x_e\right]$$

$$\boxed{E_V' - E_v = (\rho-1)E_V}$$

ρ determines the isotopic effect on the vibration energy levels (E_v')

$$\rho - 1 = \frac{E_v' - E_v}{E_v}$$

$$\boxed{\rho = 1 + \frac{E_v' - E_v}{E_v}}$$

If $\rho < 1$ than vibrational level of heaviour isotope are lower than those of lighter isotope.

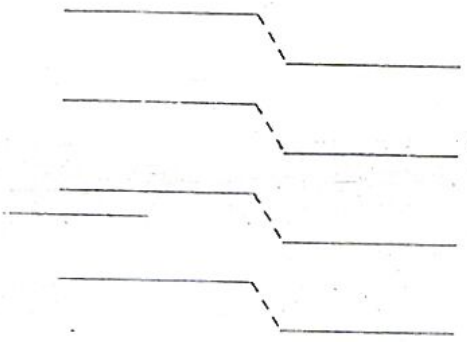
The bond belonging to $H^{35}Cl$ is shifted by a small amount toward shorter wave number with respect to corresponding band belonging ro $H^{35}Cl$ for molecule like $H^{35}Cl$ and $D^{35}Cl$.

ρ is nearly 0.7 and the shift is 80 great than the bands lie in quite different spectral region.

Heaviour molecule shift down

$$HCl = \frac{35}{36}$$

$$DCl = \frac{70}{37}$$



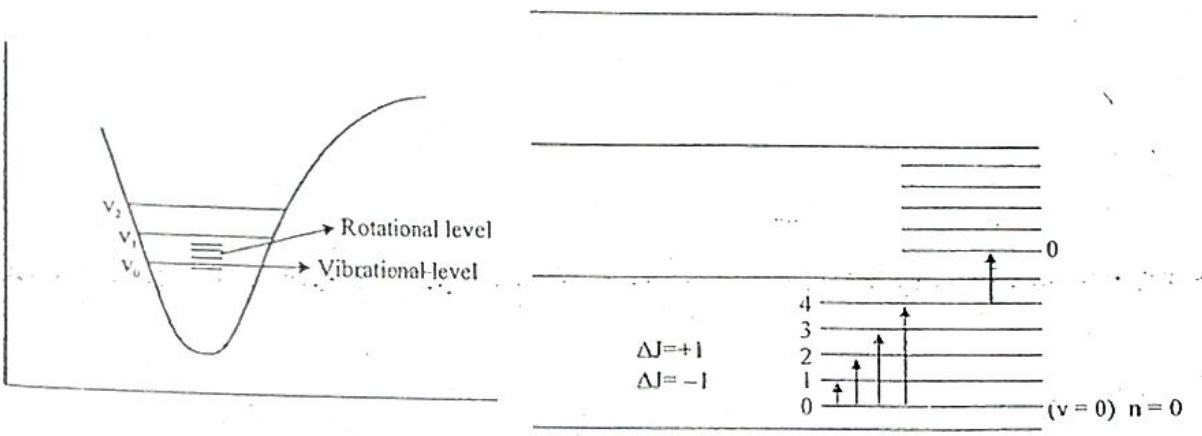
The difference is larger so the spectral region shifted

$\rho = 0.7 \rightarrow$ this show different spectral region. $\boxed{\rho < 1}$

$$\left.\begin{aligned} H^{37}Cl &= \frac{37}{38} \\ H^{35}Cl &= \frac{35}{36} \end{aligned}\right\} \rightarrow \text{This not so much difference. So, it do not show different spectral region}$$

VIBRATIONAL ROTATIONAL SPECTRA

There are number of rotational energy level associated with the vibrational level. In rotational spectroscopy we observed the transition between rotational level associated with same vibrational level (n = 0)



In vibrational rotational spectroscopy we observe transition between number of rotational energy level in associated with two different vibrational levels. These transition are applicable for all vibrational transition.

Vibrational spectra → liquid or solid

Rotational spectra → gas

Generally vibration rotational spectra us.

Generally vibration transition may be observed when the sample is in liquid or solid state. The rotation transition may be observed in gas.

So, if vibration and rotation transition may be observed so the energy of vibrational rotational is

$$E = \underbrace{\left(n+\frac{1}{2}\right)\omega_e - \left(n+\frac{1}{2}\right)^2 \omega_e x_e}_{\text{vibrational}} + \underbrace{BJ(J+1) - DJ^2(J+1)}_{\text{rotational}}$$

The rotational selection rule govering the transition.

$$\boxed{\Delta J = \pm 1}$$
$$\boxed{\Delta v = \pm 1}$$

The selectional rule for vibrational and rotational (pure) may be changed and the forbidden $\Delta J = 0$ may be allowed in vibrational rotation transition.

$$\boxed{\Delta J = 0, \pm 1}$$

Best example is "Nitric oxide"

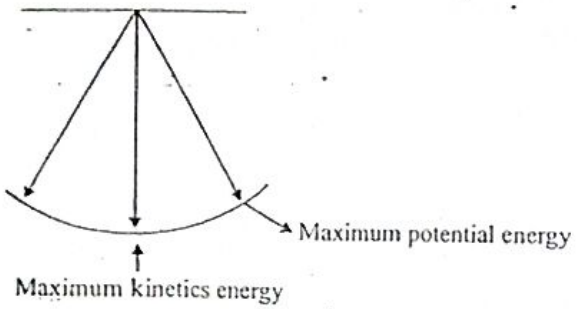
So, if we are taking anharmonic oscillator and rigid rotator than energy become

$$\boxed{E = \left(n+\frac{1}{2}\right)\omega_e + \left(n+\frac{1}{2}\right)^2 \omega_e x_e + BJ(J+1)} \qquad \Rightarrow E = \left(n+\frac{1}{2}\right)\omega_e$$

The spacing in beween the lines of I branch slowely decreases and the other branch is slowly increases as we move towards higher and higher lines of the branch. This is called "vibrational rotational interaction".

The value of B determined the spacing between the rotational levels and it is difficult for different vibrational state.

AMPLITUDE OF VIBRATION



Alceto classical mechanics:

We find from classical mechanics that letthe extreme of the vibration the total energy is positive in the form of potential energy equating the classical expression of P.E. with the vibrational energy we can find that the maximum displacement from equilibrium bond length.

$$\frac{1}{2}kx_{max}^2 = E_{vib} \quad \Rightarrow \quad \frac{1}{2}kx_{max}^2 = h\nu\left(n+\frac{1}{2}\right) h\frac{1}{2\pi}\sqrt{\frac{k}{\mu}}\left(n+\frac{1}{2}\right)$$

$$x_{max} = \sqrt{\frac{h}{\pi}}\left(\frac{1}{\sqrt{k\mu}}\right)^{1/2}\sqrt{\left(n+\frac{1}{2}\right)} \quad \Rightarrow \quad E_{vib} = \left(n+\frac{1}{2}\right)h\nu \qquad \nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

$$\Rightarrow \quad \frac{1}{2}kx_{max}^2 = h\frac{1}{2\pi}\sqrt{\frac{k}{\mu}}\left(n+\frac{1}{2}\right) \quad \Rightarrow \quad x^2\,max = \frac{h}{k\pi}\sqrt{\frac{k}{\mu}}\left(n+\frac{1}{2}\right)$$

$$\boxed{x_{max} = \sqrt{\frac{h}{\pi}}\left(\frac{1}{\sqrt{k\mu}}\right)^{1/2}\sqrt{n+\frac{1}{2}}}$$

If we take the example of HCl, $\mu = 1.615\times10^{-27}$, $k_f = 4.781\times10^2$ and the equilibrium bond length is 127 pm.

$$x_{max} = 10.2 \text{ pm}$$

It is not exactly 10% of 127 pm. So, less than 10% displacement means harmonic displacement.

We find that vibrational amplitude is 10% of the bond length such a small displacement the vibration may be consider harmonic in nature.

DISSOCIATION ENERGY OF DIATOMIC MOLECULE

The vibration energy of the molecule is increases when the vibrational quantum increased. As state is reached where vibration energy is quite sufficient to break the molecule into atom.

So, dissociation state of the molecule is that where the vibrational energy is maximum and the vibrational quantum number at this stage may be determine.

Maximum vibrational quantum number where dissociation occur (n_{max}). Dissociation occur at higher level.

$$\frac{dV}{dx} = 0$$

The value of vibrational quantum number at the dissociation state may be determine by applying mathematical criteria of maxime

$$\frac{dV}{dx} = 0$$

$$V = \left(n + \frac{1}{2}\right)\omega_e - \left(n + \frac{1}{2}\right)^2 \omega_e x_e$$

Now, differentiate this equation w.r.t. n

$$\frac{dV}{dx} = \frac{d}{dx}\left(n_{max} + \frac{1}{2}\right)\omega_e - \frac{d}{dx}\left(n_{max} + \frac{1}{2}\right)^2 \omega_e x_e$$

$$\therefore \quad \omega_e - 2\left(n_{max} + \frac{1}{2}\right)\omega_e x_e = 0$$

$$\therefore \quad \omega_e - 2n_{max}\omega_e x_e - \omega_e x_e = 0$$

$$\boxed{n_{max} = \frac{1}{2x_e} - \frac{1}{2}}$$

$$\left(n^2 + \frac{1}{4} + n\right)\omega_e x_e$$

$$n^2\omega_e x_e + n\omega_e x_e$$

$$= 2n\omega_e x_e + \omega_e x_e$$

$$= \omega_e x_e (2n + 1)$$

$$1 - 2n_{max}x_e - x_e = 0 \quad \Rightarrow \quad 2n_{max}x_e - 1 - x_e$$

$$n_{max} = \frac{1}{2x_e} - \frac{x_e}{2x_e} \quad \Rightarrow \boxed{n_{max} = \frac{1}{2x_e} - \frac{1}{2}}$$

Here, n_{max} is dependent on x_e.

n_{max} = maximum number of vibrational quantum

x_e = anharmonocity constant.

$$V_{max} = \left[n_{max} + \frac{1}{2}\right]\omega_e - \left[n_{max} + \frac{1}{2}\right]^2 \omega_e x_e$$

Put the value of n_{max}.

$$= \left[\frac{1}{2x_e} - \frac{1}{2} + \frac{1}{2}\right]\omega_e - \left[\frac{1}{2x_e} - \frac{1}{2} + \frac{1}{2}\right]^2 \omega_e x_e = \frac{1}{2x_e}\omega_e - \left(\frac{1}{2x_e}\right)^2 \omega_e x_e$$

$$= \frac{\omega_e}{2x_e} - \frac{\omega_e x_e}{4x_e} = \frac{\omega_e}{2x_e} - \frac{\omega_e}{4x_e} \quad \Rightarrow \boxed{D_e = V_{max} = \frac{\omega_e}{4x_e}}$$

$$D_0 = V_{max} - V_0 = \frac{\omega_e}{4x_e} - \left(\frac{1}{2} - \omega_e - \frac{1}{4}\omega_e x_e\right) = \frac{\omega_e}{4x_e} - \frac{\omega_e}{2} + \frac{\omega_e x_e}{4}$$

$$\boxed{D_0 = \frac{\omega_e}{4x_e} - \frac{1}{2}\omega_e\left[1 - \frac{1}{2}x_e\right]} \quad \Rightarrow \quad \boxed{D_0 = D_e - \frac{1}{2}\omega_e}$$

$$\boxed{n_{max} = v_{max} = \frac{1}{2x_e} - \frac{1}{2}}$$

SOLVED PROBLEMS

1. $J = 1 \leftarrow 0$ transition in HCl at 24.68 cm regarding the molecule to be rigid rotator. Calculate the wavelength $J = 16 \leftarrow 15$

Soln. $2B = 24.68\ cm^{-}$ $\Rightarrow B = 12.34$

$\Delta E = 2B(J+1)$ $\Rightarrow \Delta E = 2B(0+1)$

$\Rightarrow \Delta E = 2B$ $\Rightarrow \Delta E = \bar{v} = 2B(15+1)$ $\Rightarrow \Delta E = 32B = 32 \times 12.34\ cm^{-1}$

$$\lambda = \frac{1}{\bar{v}} = \frac{1}{32 \times 12.34} = \frac{1}{394.88} = 0.0025 \Rightarrow \boxed{\lambda = 0.0025\ cm}$$

DOPPLER EFFECT ON SPECTRAL LINES

It is found that spectroscopy line from the gas phase transfer are not aso sharp and the modification of line width in the gaseous phase is done by Doppler. It is essential far rotational spectroscopy that the molecule can rotate freely in gaseous phase.

To study the atmospheric science we use rotational spectra because rotational spectra is important.

Doppler effect is observed in the gaseous sample and the life time broadening may be calcualted by using Heisenberg uncertainty principle by taking standard for by stabishing the commutator relationship. Life time broadening is also called as uncertainty broadining.

Line width depend on energy.

$$\boxed{\Delta E \Delta t \geq \frac{h}{4x}} \Rightarrow \boxed{\begin{array}{l}\Delta E + \Delta t = \dfrac{h}{2} \\ \Delta E\ \Delta t = h\end{array}}$$

$$\delta E = \frac{h}{L} \Rightarrow \boxed{\Delta \bar{v} = \frac{5.3\ cm^{-1}}{\tau}} \Rightarrow \left[\Delta E = h\Delta v H_z = hc\Delta \bar{v}\ cm^{-1}\right]$$

$$\Delta E \Delta t = \hbar \Rightarrow \Delta E = \frac{\hbar}{\Delta t} \Rightarrow h\Delta v = \frac{\hbar}{\Delta t}$$

$$\Rightarrow hc\,\Delta \bar{v} = \frac{h}{\Delta t} \Rightarrow \Delta \bar{v} = \frac{h}{hc\Delta t}$$

$$\boxed{\Delta \bar{v} = \frac{5.3\ cm^{-1}}{\tau}}$$

where, $\Delta \bar{v}$ = line width, τ = Life time or uncertainty time.

2. Estimate the life time of the state that give rise to a line of width is (i) 100 MHz and (ii) 2.14 cm^{-1}.

$\Delta\bar{v} = 100\ MHz = 100\times10^{6}\ sec^{-1}$

(ii) $\Delta\bar{v} = \dfrac{5.3\ cm^{-1}}{\tau/ps} \Rightarrow \dfrac{\tau}{p-sec} = \dfrac{5.3\ cm^{-1}}{\Delta\bar{v}} = \dfrac{5.3\ cm^{-1}}{2.14\ cm^{-1}} \Rightarrow \dfrac{\tau}{p-sec} = 2.40$

(i) $\dfrac{\tau}{p-s} = \dfrac{5.31\ cm^{-1}}{\Delta\bar{v}} = \dfrac{5.31\ cm^{-1}\times3\times10^{10}\ cm/sec}{100\times10^{6}\ sec^{-1}} \Rightarrow \dfrac{\tau}{p-sec} = 15.93\times10^{2}$

$\tau = 1.593\times10^{3}\ p-sec \Rightarrow \boxed{\tau = 1.593\ n-sec}$

Problem: Esstimate the life time of state that give rise to line of width of
(i) 0.10 m^{-1} (ii) 1.0 cm^{-1}

(i) $\Delta\bar{v} = \dfrac{5.3\ cm^{-1}}{\tau/p-s} \Rightarrow \Delta\bar{v} = 0.10\ m^{-1} = \dfrac{0.10}{100\times10}\ cm^{-1} = 10^{-3}\ cm^{-1}$

$\dfrac{\tau}{p-s} = \dfrac{5.3}{10^{-3}\ cm^{-1}} = 5.3\times10^{3} \Rightarrow \boxed{\tau = 5300\ p-sec}$

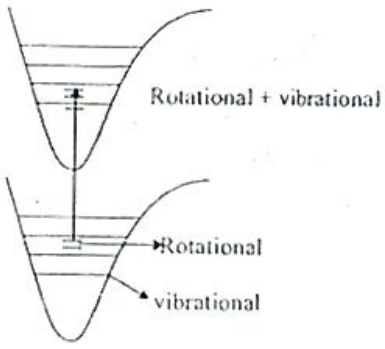
(ii) $\Delta\bar{v} = \dfrac{5.3\ cm^{-1}}{\tau/p-s} \Rightarrow \dfrac{\tau}{p-s} = \dfrac{5.3\ cm^{-1}}{1.0\ cm^{-1}} \Rightarrow \dfrac{\tau}{p-s} = 5.3$

$\boxed{\tau = 5.3\ p-sec}$

3. The ratio of life time of two states that give rise to line width of 1.0 cm^{-1} and 0.2 cm^{-1} respectively.

Soln. $\Delta v_1 \propto \dfrac{1}{\tau_1} \Rightarrow \dfrac{\Delta v_1}{\Delta v_2} = \dfrac{\tau_2}{\tau_1} \Rightarrow \dfrac{1.0}{0.2} = \dfrac{\tau_2}{\tau_1} \Rightarrow \dfrac{5}{1} = \dfrac{\tau_2}{\tau_1}$

$\boxed{\tau_1 : \tau_2 = 1:5}$ $\quad [\Delta v_1 : \Delta v_2 = 5:1]$



Energy:

$\boxed{E_{v,J} \to E_J, E_{J+1}}$ → pure rotational

$\boxed{E_{v+1,J} \to E_{v+2}, J}$ → pure vibrational

Find out energy difference ΔE for

$\boxed{E_{v,J} \to E_{v+1,J}}$ pure vibrational

$E_{v,J} \to E_{v+1}\, E_{J+1} \to$ vibrational – rotational

$$\left[E_{v,J} \to E_v\, E_{J+1}\right] \qquad \Rightarrow \quad E_{v,J} = BJ(J+1) - DJ^2(J+1)^2 + \left(v+\frac{1}{2}\right)h\nu - \left(v+\frac{1}{2}\right)hx$$

$$E_{v,J} = BJ(J+1) + \left(v+\frac{1}{2}\right)h\nu - \left(v-\frac{1}{2}\right)^2 h\nu x_e \qquad \Rightarrow v = v',\ [J = J', J' = J+1]$$

$$E_{v',J'} = B'(J+1)(J+2) + \left(V'+\frac{1}{2}\right)h\nu + \left(v'+\frac{1}{2}\right)^2 h\nu$$

$$\Delta E = B'J'(J'+1) - BJ(J+1) + G(v') - G(v)$$

$$= B'(J+1)(J+1+1) - BJ(J+1) + G(v') - G(v)$$

$$= B(J+1)(J+2) - BJ(J+1) + G(v') - G(v)$$

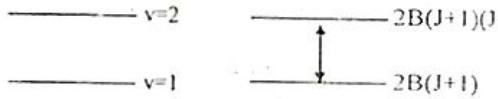
$$= B'\left(J^2+3J+2\right) - B\left(J^2+J\right) + G(v') - G(v)$$

$$\Delta E = (B'-B)\left(J^2\right) + (JB'-B)J + 2B' + G(v') - G(v)$$

$$\boxed{\Delta E = (B'-B)J^2 + (3B'-B)J + 2B' + G(v') - G(v)}$$

$$\boxed{G(v') - G(v) = \left[\left(v+1+\frac{1}{2}\right)\omega_e - \left(v+1+\frac{1}{2}\right)^2 \omega_e x_e - \left[\left(v-\frac{1}{2}\right)\omega_e - \left(v+\frac{1}{2}\right)^2 \omega_e x_e\right]\right]}$$
$$= \omega_e - 2(v+1)\omega_e x_e$$

$$\boxed{\Delta E = (B'-B)J^2 + (3B'-B)J + 2B' + \omega_e - 2(v+1)\omega_e x_e}$$



$E_2 - E_1 \Rightarrow \Delta E = 2B(J+1)$

4. Calculate the value of ρ. The fundamental mode of HCl occurs at 2886 cm^{-1} predical the frequency of DCl and ρ.

Soln. $\bar{\nu} = \omega_e = 2886\ cm^{-1} \quad \Rightarrow \mu = \dfrac{1\times 35}{1+35} = \dfrac{35}{36}$

$$\Rightarrow \mu' = \frac{2\times 35}{2+35} \qquad \Rightarrow \mu' = \frac{70}{37}$$

$$\frac{\omega'}{\omega} = \frac{\nu'}{\nu} = \sqrt{\frac{\mu}{\mu'}} = \rho \qquad \Rightarrow \rho = \sqrt{\frac{\frac{35}{36}}{\frac{70}{37}}} \qquad \rho = \sqrt{\frac{35}{36}\times\frac{37}{10}} = \sqrt{0.51} \qquad \Rightarrow \boxed{\rho = 0.71}$$

$\omega' = \rho\omega = 0.7\times 2886 \Rightarrow \boxed{\omega' = 2020.8\ cm^{-1}}$

D = centrifugal distortion.

PURE VIBRATIONAL SPECTRA

$$E = \left(v + \frac{1}{2}\right)h\nu \qquad \Rightarrow \nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad \text{where, } k = \text{force constant } \frac{N}{m}$$

$$\frac{kg}{\text{molecule}} \rightarrow \mu = \frac{m_1 m_2}{m_1 + m_2} \times \frac{10^{-3}}{N_A} = \frac{m_1 m_2}{m_1 + m_2} \times 1.67 \times 10^{-27} \text{ kg / molecular}$$

If anharmonicity introduce

$$E = \left(v + \frac{1}{2}\right)h\nu - \left(v + \frac{1}{2}\right)^2 h\nu x_e \qquad \text{where, } x_e = \text{anharmonicity constant}$$

$$E = \left(v + \frac{1}{2}\right)\omega_e - \left(v + \frac{1}{2}\right)^2 x_e\omega_e$$

$$E_1 - E_0 = \omega_e(1 - 2x_e) = \omega_e - 2\omega_e x_e \qquad \Rightarrow E_2 - E_0 = 2\omega_e(1 - 3x_e) = 2\omega_e - 6\omega_e x_e$$

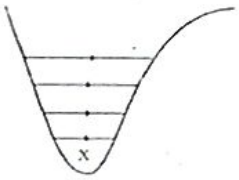
Anharmonic oscillator, $E_0 = \frac{1}{2}\omega_e - \frac{1}{4}\omega_e x_e = \frac{1}{2}h\nu - \frac{1}{2}h\nu x_e$

Dissociation $= \nu_{max} - \nu_0$

$$V_{max} = \frac{1}{2x_e} - \frac{1}{2} \qquad \Rightarrow E = \left(\nu_{max} + \frac{1}{2}\right)h\nu - \left(\nu_{max} + \frac{1}{2}\right)^2 h\nu x_e$$

$$E = \left[\left(\frac{1}{2x_e} - \frac{1}{2} + \frac{1}{2}\right)h\nu - \left(\frac{1}{2x_e} - \frac{1}{2} + \frac{1}{2}\right)^2\right]k\nu x_e \qquad \Rightarrow E = \frac{h\nu}{2x_e} - \frac{h\nu}{4x_e}$$

$$\left(B = \frac{h}{8\pi^2\omega_e r_e^2 c}\right)$$



$$B \propto \frac{i}{r_2^2}$$

B also vary when we use V = 0, V = 1, V = 2. If r_e increases than B decreases and V increases.

Rotational vibrational spectra:

$$= \underbrace{BJ(J+1) - DJ^2(J+1)^2}_{\text{non-rigid}} + \underbrace{h\nu\left(v + \frac{1}{2}\right) - \left(v + \frac{1}{2}\right)^2 h\nu x_e}_{\text{anharmonic}} \qquad \Rightarrow E_{v,J} = \underbrace{BJ(J+1)}_{\text{rigid}} + \underbrace{h\nu\left(v + \frac{1}{2}\right)}_{\text{harmonic}}$$

$$E_{v+1,J+1} - E_{v,J} = \left[B'(J+1)(J+2) + h\nu\left(v + 1 + \frac{1}{2}\right) - \left(BJ(J+1) + h\nu\left(v + \frac{1}{2}\right)\right)\right]$$

$$= B'\left(J^2 + 3J + 2\right) + h\nu\left(v + \frac{1}{2} + 1\right) - B\left(J^2 + J\right) - h\nu\left(v + \frac{1}{2}\right)$$

$$= (B' - B)J^2 + (3B' - B)J + 2B' + h\nu$$

$$\boxed{B' < B}$$

Rigid simple harmonic:

$E_{v'J'} - E_{v''J''}$

Selection P, Q, R branches of spectra.

$\Delta J = +1$		$\Delta J = -1$	$\Delta J = 0$	$\Delta J = +1$	$\Delta J = \pm 1$ (Selection rule for Raman)
$\Delta J = -1$	−2	−1	0	+1	+2
$\Delta J = 0$	O	P	Q	R	S
		On P line	On Q line		For Raman

$\Delta J = J' - J''$

$-1 = J' - J''$ $\quad J' - J'' =$ rotational level distance

$J'' = J' + 1$

$J' - J'' = \Delta J$

$J' - J'' = +1 \quad \Rightarrow J'' = J' - 1$

$J' - J'' = -1 \quad \Rightarrow J'' = J' + 1$

$J' - J'' = 0 \quad \Rightarrow J' = J''$

All lines of intensity vary in vibrational rotational spectrum.

To know which intensity is weak $(J' = J'')$

$\Delta v = +1 + 2, +3$ → Ignored because intensity will be weak these are overtone so forbidden

[First overtone, Second overtone] Hotbands

$B << D$

In same vibration than only pure rotation but vibration rotation is in different rotation level.

We find from the sake of the potential cure as 'v' increases the equilibrium internuclear separation increases moment of inertia increases. Rotational constant (B) decreases. Thus B which determine the spacing between the rotation level is different for different vibrational state. So, internuclear distance and the rotational constant is changing during the vibration so we may take the mean value of the rotation constant also.

$$B_v = \frac{h}{8\pi^2 \mu}\left(\frac{1}{r^2}\right)$$

Where, B_v = Mean value.

Because rotational constant is changing with vibrational level and depend upon the shape of the rotational curve B_v is also dependent on B_e.

$$B_v = B_e - \alpha\left(v + \frac{1}{2}\right).....$$

B_e = rotational constant at minimum level

$$B_e = \frac{h}{8\pi^2 \mu r_e^2 c}$$

When, $v = 1$

$$B_v = B_e - \alpha\left(1 + \frac{1}{2}\right) \quad \Rightarrow B_v = B_e - \frac{3}{2}\alpha$$

When, $v = 2$

$$B_v = B_e\alpha\left(2+\frac{1}{2}\right) \quad \Rightarrow B_v = B_e - \frac{5}{2}\alpha$$

$[\alpha << B_e]$

α = constant it depend on shape of potential curve set.
The value of α dependent on shape of potential curve.
So, B_v decreases slightly with increases 'v' the selection rule.

Selection rule:

For J both the transition $\Delta J = \pm 1$ are now applicable in absorption because two J level involved now belongs to two vibrational level. For a given vibrational transition the rotational transition $\Delta J = +1$ give one set of line i.e. has called as R branch.

When the rotational vibration $\Delta J = -1$ give another set of lines i.e. P branch and the Q branch consist of all lines with $\Delta J = 0$. It is also called as Band origin (v_0)

$$E_{v',J'} - E_{v'',J''} = (E_{v'} - E_{v''}) + B'J'(J'+1) - B''(J'')(J''+1)$$

$$\boxed{\Delta E = v_0 + B'J'(J'+1) - B''(J'')(J''+1)}$$

$B' = B''$ (not so much difference in B' and B")

In Q branch: $J'' = J'' \quad \Rightarrow B' = B''$

$\boxed{\Delta E = v_0}$. It is called Band orogin.

$J' = J'' \quad \Rightarrow J' - J'' = 1$

$\Delta J = +1$

In Q branch: If $B' \neq B'' \quad \Rightarrow J' = J''$

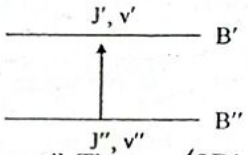
$$\boxed{\Delta E_Q = V_0 + (B' - B'')J'(J'+1)} \quad \Rightarrow \boxed{\Delta E_Q = V_0 + (B' - B'')J''(J''+1)}$$

If $J'' = 0$, than $\boxed{\Delta E_Q = v_0}$

In P branch:

$\Delta J = -1 \quad J' - J'' = -1$

$J' = J'' - 1$



$(B' - B'')$ is always negative value though very small. The term $(3B' - B'')$ is positive as B' is only slightly smaller than B".

So, the linear and square (quadrate) term are opposite in sign (+ve or –ve) J" is the lower rotation number. This can take the value (0, 1, 2, 3 .....so all lines are found $R_{(0)}, R_{(1)}, R_{(2)}$.

$R_{(0)} \Rightarrow \Delta E = v_0 + 2B'$

$R_{(0)}$	$R_{(1)}$	$R_{(2)}$	----
$J'' = 0$	$J'' = (1)$	$J'' = 2$	

1. When $B' \neq B''$

$$R_{(0)} = v_0 + 0^2(B' - B'') + (3B' - B'')0 + 2B'$$

$$\boxed{R_{(0)} = v_0 + 2B'}$$

$$R_{(1)} = v_0 + (1)^2 + (B' - B'') + (3B' - B'')1 + 2B''$$

$$\boxed{R_1 = v_0 + 6B' - 2B''}$$

$$R_{(2)} = v_0 + (2)^2 (B' - B'') + (3B' - B'')(2) + 2B'$$

$$R_2 = v_0 + 4B' - 4B'' + 6B' - 2B'' + 2B'$$

$$\boxed{R_2 = v_0 + 12B' - 6B''}$$

Hence hte line spacing decreases very slowly as J'' increases if $B' = B''$

2. When $B' = B''$

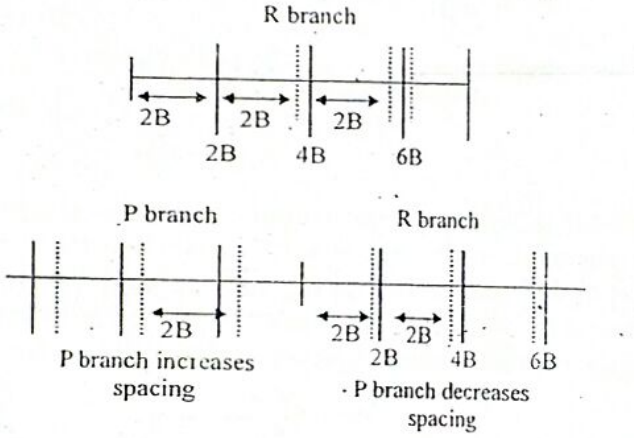
Than $\Delta E = v_0 + 2B'J'' + 2B''$

$$\Delta E = v_0 + 2B''J'' + 2B''$$

$$\Delta E = v_0 + 2B(J'' + 1)$$

$$\boxed{R_{(0)} = v_0 + 2B} \quad \Rightarrow \boxed{R_{(1)} = v_0 + 4B} \quad \Rightarrow \boxed{R_{(2)} = v_0 + 6B}$$

When $B' = B''$ but it is not exactly square so some difference comes out.



P- branch:

$$\Delta J = -1 \quad \Rightarrow J' - J'' = -1 \quad \boxed{J' = J'' - 1}$$

$$\Delta E = v_0 + B'J'(J' + 1) - B''J''(J'' + 1) \quad \Rightarrow \Delta E = v_0 + B'(J'' - 1)(J'') - B''J''(J'' + 1)$$

$$\Delta E = v_0 + (B' - B'')J''^2 - (B' + B'')J''$$

$$\Downarrow$$

$$0$$

If $B' = B''$, than $\Delta E = v_0 - 2B''J''$

$$\boxed{\Delta E = v_0 - 2BJ''} \quad \Rightarrow \boxed{\Delta E = -2BJ''}$$

For P branch $[\Delta J = -1]$, So, J'' is the lower rotational quantum number can take value 1, 2, 3 and so on (J'' can not be zero because the level ($J' = -1$) does not exist)

Thus, P branch consist of a series of a line $P_{(1)}, P_{(2)}, P_{(3)}$

If $B' = B''$ than $\boxed{P_{(1)} = \nu_0 - 2B}$

$\boxed{P_2 = \nu_0 - 4B}$

$\boxed{P_3 = \nu_0 - 6B}$

$$\Delta E = \nu_0 + \underset{\text{negative value}}{\underset{\downarrow}{(B'-B'')}} J''^2 - \underset{\text{negative value}}{\underset{\downarrow}{(B'-B'')}} J''$$

Quadrative and linear part are now of the same sign (-ve) so the line pattern of the P is different than R pattern. If we neglect vibrational rotational interaction the wave number of

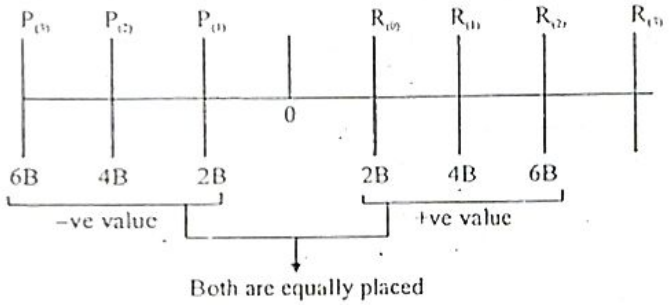
$$\nu_R = \nu_0 + 2B(J''+1) = \nu_0 + 2B + 2BJ''$$

$\boxed{\nu_R = \nu_0 + 2B + 2BJ''}$

$\boxed{\nu_P = \nu_0 - 2BJ''}$

ν_R and ν_P are equally space.

$\boxed{\nu_Q = \nu_0}$



$\boxed{\Delta E = \nu_R = \nu_0 + (B'-B'')J''^2 + (3B'-B'')J'' + 2B''}$

$\boxed{\Delta E = \nu_P = \nu_0 - (B'+B'')J'' + (B'-B'')J''^2}$

$\boxed{\Delta E = \nu_Q = \nu_0}$

The exact equation for both branches may be fit to this equation

$\boxed{\nu = \nu_0 + (B'+B'')m + (B'-B'')m^2}$ ... (i)

$m = (J''+1)$ for R line

$\boxed{m = -J'' \text{ for P line}}$

$\boxed{m = 0 \text{ for Q line}}$

If we put the 'm' value in equation (i)

Than, $\nu_R = \nu_0 + (B'+B'')(J''+1) + (B'-B'')(J''+1)^2$

$= \nu_0 + (BJ'' + B' + B''J'' + B'') + (B'-B'')(J''^2 + 2J'' + 1)$

$$= v_0 + \left(B'J'' + B' + B''J'' + B''\right) + \left(B'J''^2 + 2B'J'' + B' - B''J''^2 - B''\right)$$

$$= v_0 + \left(B'J'' + B' + B''J'' + B'' + B'J''^3 + 2B'J'' + B' - B''J''^2 - 2B''J'' - B''\right)$$

$$= v_0 + 2B' + 3B'J'' - B''J'' + B'J''^2 - B''J''^2$$

$$= v_0 + 2B' + 3B'J'' + B'J''^2 - B''J'' - B''J''^2$$

$$= v_0 + 2B' + 3B'J'' - B''J'' + B'J''^2 - B''J''^2$$

$$= v_0 + 2B' + (3B' - B'')J'' + J''^2(B' - B'')$$

$$\boxed{\Delta E = v_0 + (B' - B'')J''^2 + J''(3B' - B'') + 2B'}$$

Problem: Find the amplitude of vibration of HCl molecule in the first excited vibrational level the force constant k = 480 N/m.

$$\mu = 1.67 \times 10^{-27}$$

$$x_{max} = \sqrt{\frac{h}{\pi}} \times \left(\frac{1}{\sqrt{k\mu}}\right)^{1/2} \sqrt{\frac{n+1}{2}} = \sqrt{\frac{6.6 \times 10^{-34}}{3.14}} \times \left(\frac{1}{\sqrt{480 \times 1.67 \times 10^{-27}}}\right)^{1/2} \sqrt{\frac{1+1}{2}}$$

$$= \sqrt{2.10 \times 10^{-34}} \times \left(\frac{1}{\sqrt{80.16 \times 10^{-27}}}\right)^{1/2} \times \sqrt{\frac{2+1}{2}} = 1.449 \times 10^{-17} \times \left(\frac{1}{28.3 \times 10^{-27}}\right)^{1/2} \times \sqrt{\frac{3}{2}}$$

$$= 1.449 \times 10^{-17} \times \sqrt{\frac{0.035 \times 10^{27}}{1000}} \times \sqrt{1.5} = 1.449 \times 10^{-17} \times \sqrt{35 \times 10^{24}} \times 1.22$$

$$= 1.449 \times 10^{-17} \times 10^{12} \times 5.916 \times 1.22 = 10.45 \times 10^{-5}.$$

THERMAL DISTRIBUTION OF VIBRATION & ROTATIONAL LEVEL

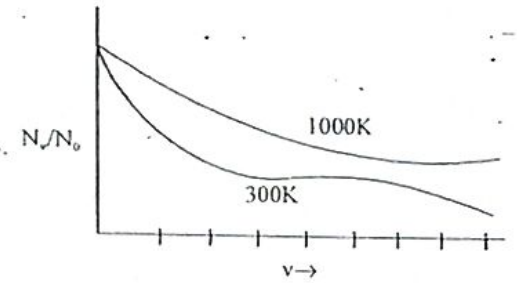
According to Maxwell Boltzmann

$$\frac{N_V}{N_0} = e^{-(E_V - E_0)/kT}$$

So, in this effect of temperature.

$$E_v = \left(v + \frac{1}{2}\right)\omega_e - \left(v + \frac{1}{2}\right)^2 \omega_e x_e$$

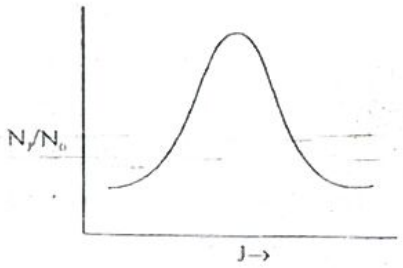
If we plote a graph between $\frac{N_V}{N_0}$ and the vibrational quantum number 'v' for I_2 molecule at a particular temperature 300 K and 1000 K at the room temperature the population of higher vibrational level is very small compaired to the lowest level. It is still smaller even at higher temperature for lighter molecule. Heaviest diatomic molecule has an appreciable population in vibrational spectra and the graph $\frac{N_V}{N_0}$



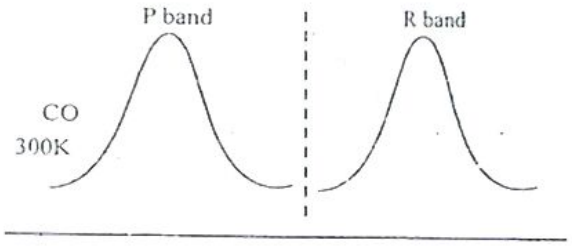
If we increase temperature than N_v/N_0 increases. $(E_v - E_e)$ decreases than N_v/N_0 increases and μ increases.

$$\frac{N_J}{N_0} = (2J+1)e^{-BJ(J+1)/kT}$$

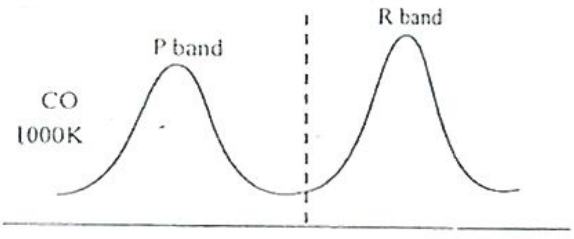
When we plot a graph of N_J/N_0 v/s J for CO molecule.



If we dissecused R and P branched in the absorption band R branch stronger than P branch reverses in the case of emission band.



$$V_R^{max} - V_P^{max} = +ve$$



Some peak is decreases when we increases temperature but the R is always greater than P (at 1000K)

$$V_R = v_0 + 2B(J+1)$$

$$\boxed{v_R \text{ max} = v_0 + 2B(J_{max}+1)} \quad \ldots (i)$$

$$\left[\begin{array}{l} J_{max} = \sqrt{\frac{kT}{2B}} - \frac{1}{2} \\ J_{max} = \sqrt{\frac{kT}{2Bhc}} - \frac{1}{2} \end{array}\right].$$

Put the value of J_{max} in above equation (i)

$$V_R \text{ max} = v_0 + 2B\left(\sqrt{\frac{kT}{2Bhc}} - \frac{1}{2} + 1\right) = v_0 + 2B\sqrt{\frac{kT}{2Bhc}} - \frac{1}{2}$$

$$\boxed{V_P = v_0 - 2BJ}$$

$$\boxed{V_{p\,max} = v_0 - 2BJ_{max}} \quad \text{... (ii)}$$

Put the value of J_{max} in equation (2)

$$V_{p\,max} = v_0 - 2B\left[2B\sqrt{\frac{kT}{2Bhc}} - \frac{1}{2}\right]$$

$$V_{R\,max} - V_{P\,max} = v_0 + 2B\left[2B\sqrt{\frac{kT}{2Bhc}} - \frac{1}{2}\right] - \left[v_0 - 2B\left(2B\sqrt{\frac{kT}{2Bhc}} - \frac{1}{2}\right)\right]$$

$$= v_0 + 2B\left(2B\sqrt{\frac{kT}{2Bhc}} - \frac{1}{2}\right) - v_0 + 2B\left(2B\sqrt{\frac{kT}{2Bhc}} - \frac{2B}{2}\right)$$

Problem: The rotation vibration spectrum of HCl gas shows a number of lines centred about the fundamental vibration band the few of which have the wave number 2847 cm–1, 2866 cm–1, 2906 cm–1 and 2927 cm–1, using this data calculate the bond length, force constant and anharmonicity, constant for HCl.

Soln. $2.906\times10^5 = \omega_0 + (2B)\times1$ ... (1)

$2.927\times10^5 = \omega_0 + 2B\times2$ ... (2)

Now, substracting equation (1) from equation (2), we get

$$2.927\times10^5 = \omega_0 + 4B$$
$$\underline{2.906\times10^5 = \omega_0 + 2B}$$
$$0.021\times10^5 = 2B$$

Or, $B = \frac{0.021\times10^5}{2}$ $\quad\therefore\quad B = 0.0105\times10^5\ m^{-1}$

Or, $B = 10.5\times10^2\ m^{-1}$

We know that, $B = \frac{h}{8\pi^2 Ic}$. So, $I = \frac{h}{8\pi^2 Bc}$

Now, putting the value of h, π, B *and* C we get the value of moment of inertia.

$$I = \frac{6.624\times10^{-34}\ J-s}{8\times3.14\times10.5\times10^{10}\ s^{-1}} = \frac{6.624\times10^{-44}}{248.619}\ Js^2 = \frac{6.624\times10^{-44}}{24\times3.14\times3.14\times10.5}\ Js^2 = \frac{6.624}{2.484}\times10^{-47}\ Js^2$$

$I = 2.666\times10^{-47}\ Js^2$

Since, $1J = 1\ kg\ m^2 s^{-2}$

So, $\boxed{I = 2.666\times10^{-4}\ kg\ m^2}$

We know that, $I = \mu r^2$

Or, $r = \left(\frac{1}{\mu}\right)^{1/2}$ ....(A)

$\mu_{HCl} = \frac{m_1 m_2}{m_1 + m_2} = \frac{1\times35.5}{35.5+1} = \frac{35.5}{36.5}\ amu = 0.97\ amu = 0.97\times1.66\times10^{-27}\ kg$

$\mu_{HCl} = 1.614\times10^{-27}\ kg$

Now, substituting the value of μ_{HCl} and I in above expression we get required condition,

$r = \left(\frac{2.666\times10^{-47}\ kgm^2}{1.614\times10^{-27}\ kg}\right)^{1/2} \Rightarrow r = \left(\frac{2.666\times10^{-20}}{1.614}m^2\right)^{1/2}$

$r = \left(1.6522\times10^{-20}\ m^2\right)^{1/2} \Rightarrow r = 1.28\times10^{-10}\ m$

$\therefore \quad r = 1.28\ \mathring{A}$

IMPORTANT GROUP FREQUENCIES :

Alkanes :

C – H str. 2850 – 3000 cm^{-1}

sp^3 C – H	2850 – 3000	cm^{-1}
sp2 C – H	3000 – 3100	cm^{-1}
sp C – H	3100 – 3300	cm^{-1}
aromatic C – H	3000 – 3050	cm^{-1}
aldehyde C – H	2750, 2850 doublet	

C – C 800 – 1300cm^{-1} (weak)

due to e$^-$negativity difference

C – C	800 – 1300	cm^{-1}
C – C → aromatic	1450 – 1600	cm^{-1}
C = C	1640 – 1675	cm^{-1}
C ≡ C	2100 – 2200	cm^{-1}

Alkenes :

= C – H str.	3000 – 3100	cm^{-1}
C = C	1640 – 1675	cm^{-1}

C–H out of plane.

bonding vib. is imp. to distinguish to geometrical isomers.

R–CH = CHR

cis 675 – 725 cm^{-1}

trans 960 – 970 cm^{-1}.

Alkynes :

$\equiv C-H$ str. $3300 \cdot$ cm^{-1}

$C \equiv C \rightarrow$ $2100-2200\ cm^{-1}$

Aromatic Hydrocarbon $\rightarrow 3000-3050\ cm^{-1}$

C=======C	1600 1580 1500 1450	Benzene ring	This is most characteristic & appear as 4 peaks for benzene ring

C – H bond in out of plane is use for identify substitution on Benzene ring.

monosubstituted doublet

(i) 710-690 cm^{-1}

(ii) 770-750 cm^{-1}

Mata	–	doublet 710 – 690 cm^{-1} 770 – 730 cm^{-1}
Ortho		singlet 770 – 735 cm^{-1}
para		singlet 840 – 800 cm^{-1}

Alcohols/Phenols :

O–H str.

Free H-bonded 3500–3700 intra H bonded

3200–3400 inter H bonded 3400–3550

1° doublet (i) 1350 – 1260 cm^{-1}

(ii) 1100 cm^{-1}

3° doublet (i) 1400–1300 cm^{-1}

(ii) 1150 cm^{-1}

1°, 2°, & 3° alcohol can be distinguish on the basis of C–O streching frequency

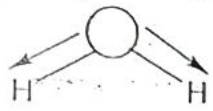
ETHERS : Only one characteristic bond in the region 1150 – 1050 cm^{-1} for assymmetric C–O streching.

FUNDAMENTAL VIBRATIONS AND THEIR SYMMETRY

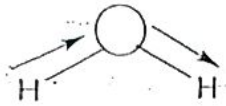
3N identity

	Translational	Rotational	Vibrational
Linear	3	2	3N–5
Non-Linear	3	3	3N–6

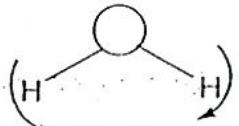
Example. : H_2O $3N - 6;\ 9-6 = 3$



Symmetri Ctrech



Assymmetric Stretching



Bending

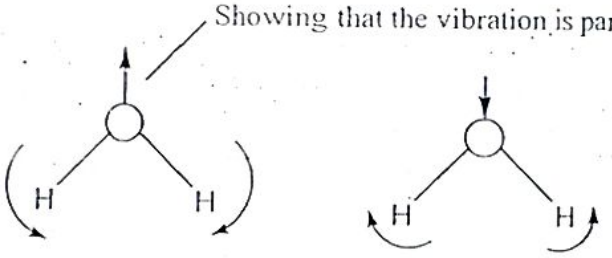
A. **On the basis of dipole direction change**

Parallel vibration — Perpendicular vibration

PARALLEL VIBRATION : Molecular vibration in which dipole moment changes along the molecular axis or dipolar axis are known as parallel vibration.

Perpendicular Vibration → On the other hand if dipole changes are not parallel to the molecular axis or to the dipolar axis the vibration is known as perpendicular vibration.

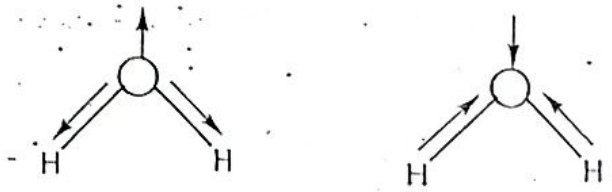
Bending :



Parallel vib. 1595. 0 cm^{-1}

Stretching :

Perpendicular vibration (I) 3755.8 cm^{-1}



Parallel (II) 3651.7 cm^{-1}

Problem. Draw the fundamental vibration of CO_2. Classify the parpendicular and parallel vibration.

CO_2 = $3N - 5$

$3 \times 3 - 5$

$9 - 5 = 4$ Total vibration.

assymmetric strech Symmetric stretch (dipole not change so I R inactive)

Linear vibrating rotator :

The energy levels will be equal to the

$$\epsilon_{J,\upsilon} = BJ(J+1) + \left(\upsilon + \frac{1}{2}\right)\bar{\omega}_e - x_e\left(\upsilon + \frac{1}{2}\right)^2 \bar{\omega}_e$$

Selection rule for paralled (II) vibration :

$\Delta\upsilon = \pm 1, \pm 2 \pm 3...$

$\Delta J = \pm 1$

only P and R line will appear Q line will be absent.

Selection rule for perpendicular vibration :

$\Delta\upsilon = \pm 1, \pm 2 \pm 3...$

$\Delta J = 0, \pm 1$

P, Q & R line will appear.

SYMMETRIC TOP MOLECULES :

$$\epsilon_{J\upsilon} = BJ(J+1) + (A-B)K^2 + \left(\upsilon + \tfrac{1}{2}\right)\bar{\omega}_e - \left(\upsilon + \tfrac{1}{2}\right)^2 x_e \bar{\omega}_e$$

Selection Rule :

For parallel (II)

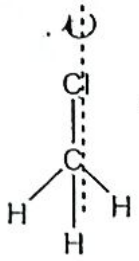
$\Delta\upsilon = \pm 1;$ $\Delta J = 0 \pm 1;$ $\Delta K = 0$

P, Q and R lines will appear.

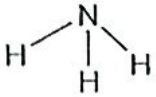
For perpendicular ($\perp$) vibration.

$\Delta\upsilon = \pm 1;$ $\Delta J = 0, \pm 1;$ $\Delta K = \pm 1$

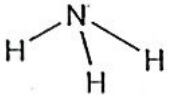
P, Q and R branch lines will appear.



I.R. inactive
$\Delta K = 0$

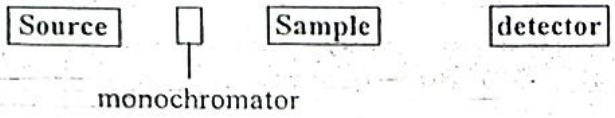


Symmetric
parallel vibration K = 0



dipole change
$K = \pm 1$
μ flactuate

INSTRUMENTATION



(1) **SOURCE :**

Source in I.R. usually consists of solids heated between 1500 – 2200 K to give black body IR radiation.

(i) **Nernst Glower :**

It composed of rare earth metal oxide and having –ve temp. coefficient of electrical resistance. This is the best source for F.T.I.R.

(ii) **Globar Source :**

It is made up of silicon carbide rode and having + ve coefficient of resistance.

(iii) **Mercury Arc Lamp :**

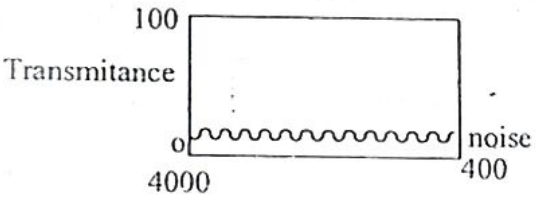
This is a very good source for far I.R.

(iv) **Tunguston Filament :**

This is very good source for near I.R.

(2) **DETECTOR :**

The detector in the I.R. spectroscopy are based on the heating effect of IR. radiation.



In the modern FT-I.R. instrument pyroelectric detectors are used in which a pyroelectric material is sandwich between two I.R. transparent electrodes to make a capacitor and the current passing capacity from this capacitor depend on the temp. of pyroelectric material. These detectors are highly sensitive for temperature change. The pyroelectric material mainly used for this purpose is Duterated riglycine sulphate mixed with alanine.

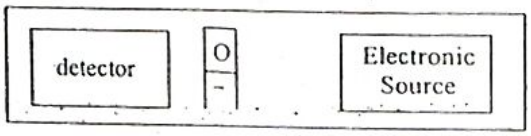
(3) SAMPLE CELL AND SAMPLING :

Window Material : The all material which passes radiation from source to detector is known as window material Glass, quartz and metal has property to absorb the I.R. radiation and these material can not be use the window material in the I.R. spectrometer, for the purpose of window material alkali metal halides are used as a window material eg :-KI, KBr, NaI, NaBr, NaCl,

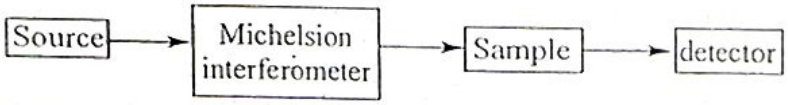
↓

less hygroscopic nature

Among all these alkali salt KBr has least hygroscopic nature hence this is used as a popular window material for I.R. spectroscopy.

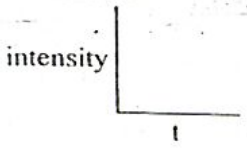


F.T.I.R.

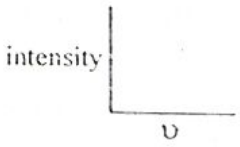


Michelsion interferometer

Time domain spectrum-

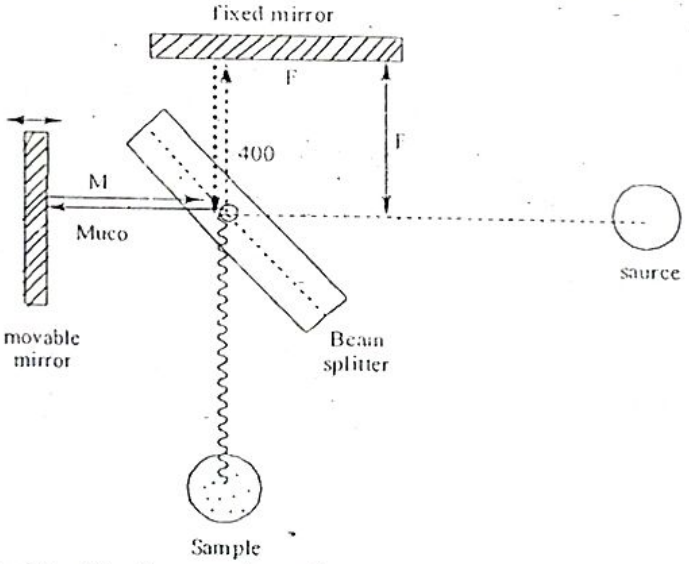


Frequency domain spectrum



In F.T.I.R instrument first observe the time domain spectrum and the computer by mathematical calculation converts it into frequency domain spectrum which appears on the window of computer.

There is no need of monochromator in the F.T.I.R. i.e. 400-4000 vibration create in one time & then relaxed.



Michelsion interferometer is consists of 2 mirrors and one beam splitter one mirror is fixed F and another is movable M.

The I.R. radiation comming from source splits into 2 equal beams and goes to the respective mirror from there it comes back to the beam splitter and interference of 2 beams of I.R. radiation takes place After interferance the radiation goes to the sample condition of interferance constructive & destructive) depend on the path difference of 2 beam i.e. equal ot the path difference = 2 (M-F)

If this path difference is equal to the integral multiple of λ then there will be constructive interference on the sample and if this path difference is half intergral multiple of λ then destructive interference on the sample.

If the speed of mirror moves at the distance $\lambda/2$ in T time then $\boxed{V_m T = \lambda/2}$ and $1/T$ = frequency F

then $\boxed{\frac{V_m}{f} = \lambda/2}$ $\boxed{f = Vm/\lambda/2 = \frac{2Vm}{\lambda}}$

$\boxed{f = 2Vm \times \bar{\upsilon}\left(cm^{-1}\right)}$

ADVANTAGE OF F.T. :

(1) **Throughput or Jaquinot advantage :**
The power of radiation that reaches the detector is much greater than disperive instrument. This increases signal to noise ratio.

(2) **Multiplex Advantage OR Fellgett Advantage :**
All the frequencies of source reaches the detector simultaneously. This characteristic make possible to obtain data for an entire spectrum in 1 second or less.

GROUP FREQUENCIES :

(1) **Carbonyl Group :** >C=0 1650–1800 cm^{-1}

1700 mid po int.

Factor affect carbonyl frequency

+I effect decreases the carbonyl frequencies.

+I effect	CH_3CHO	CH_3COCH_3
HCHO	1745 cm^{-1}	1718 cm^{-1}
1750 cm^{-1}		

(2) **–I effect :**

Increases the CO frequencies

CH_3COCH_3	CH_3COCH_2Cl	$CH_3COCHCl_2$
1718 cm^{-1}	1725 cm^{-1}	1740 cm^{-1}

Decrease in the ring size in cyclic carbonyl compound increases the CO frequencies

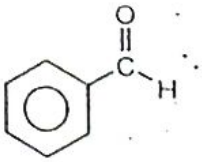
1855 1788 1746 1720

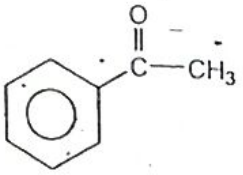
Conjugation : Conjugation decreases the carbonyl frequencies

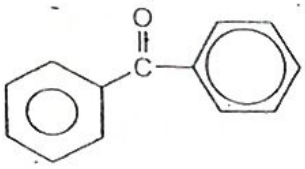
CH_3CHO $CH_2=CHCHO$ $CH_2=C(CH_3)-CHO$

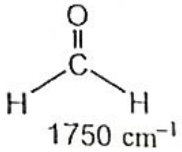
1745 cm^{-1} 1723 cm^{-1} 1702 cm^{-1}

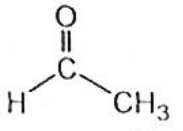
Carbonyl absorption for aryl carbonyl compound is lower than alkyl carbonyl compound due to conjugation.


1705 cm^{-1}


1665 cm^{-1}


1690 cm^{-1}


1750 cm^{-1}


1745 cm^{-1}

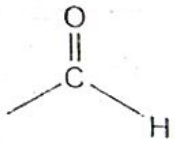
ALDEHYDES :

C=O str. 1720 – 1740 cm^{-1}

C–H str. doublet 2820 – 2900 cm^{-1} $\Delta\bar{\nabla} \approx 100\ cm^{-1}$

2720 – 2770 cm^{-1}

The C–H str. of aldehyde shows doublet due to Fermi resonance between C–H str. and C–H bend.


bend 1400 cm^{-1}

Fermi resonance $\Longrightarrow$ coupling between
(i) fundamental
(ii) overtone

Fermiresonance is coupling between a fundamental frequency and overtone of another frequency

C = O strech.

aldehyde	1720 – 1740	acid	1700 – 1725
Ketone	1700 – 1725	anhydride double	1800 – 1850
ester	1735 – 1750		1740 – 1790

Amide 1630–1690 (always less than 1700)

3° = 1630 – 1670; 2° = 1640 – 1680; 1° = 1650 – 1690

Ketone : >C=0 1700–1725 cm^{-1}

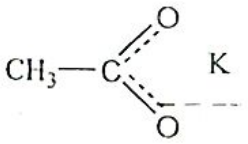
Ester : > C = 0 str. 1735 – 1750 cm^{-1}

C–O 1200–1300 cm^{-1}

Acid : > C = 0 1700 – 1725 cm^{-1}

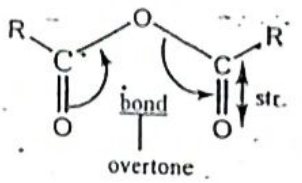
O–H str. 3500–3600 cm^{-1}

* **Carbonylate ion :**

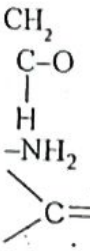

1550–1610 cm^{-1}

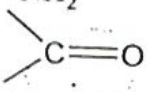
Anhydride : > C = 0 1850 – 1800 cm^{-1} doublet appears due to again fermmi resonance of

1790 – 1740 cm^{-1}



CX_2 doublet eg :



(1) Amide I bond is  streching

$1630 - 1690\ cm^{-1}$

always less than 1700

(2) Amide II bond is N–H bending

Just right to amide I bond

1° amide $1620 - 1590\ cm^{-1}$

2° amide $1550 - 1510\ cm^{-1}$

(3) Amide III bond is N–H strech: $3300–3500\ cm^{-1}$

AMINES :

(1) N–H	strech	$3300 - 3500\ cm^{-1}$
(2) N–H	bend	$1560 - 1650\ cm^{-1}$
(3) C–N	strech	$1030 - 1230\ cm^{-1}$

HETEROCOMPOUNDS :

Nitro Compounds :

	doublet	$1535 - 1620\ cm^{-1}$
		$1275 - 1375\ cm^{-1}$
Nitriles:	–C≡N	$2200 - 2300\ cm^{-1}$

SOLVED PROBLEMS

1. Which of the following spectroscopic techniques will be useful to distinguish between M-SCN and M-NCS binding modes? **[NET-June 2011]**

(a) NMR (b) IR (c) EPR (d) Mass

Soln.

CN bond stretching at higher frequency (wave number)

CN bond stretching at lower frequency(wave number)

Correct answer: (b)

2. The Q band in the vibrational spectrum of acetylene is observed in the [NET-June 2011]

(a) C–C stretching mode
(b) C-H symmetric stretching mode
(c) Bending mode
(d) C-H antisymmetric stretching mode.

Soln. Q-band (or PQR contour) is obtained for the bending vibration of C_2H_2 when its linearity is lost.

Correct answer: (c)

3. A molecule, AX, has a vibrational energy of 1000 cm^{-1} and rotational energy of 10 cm^{-1}. Another molecule, BX, has a vibrational energy of 400 cm^{-1} and rotational energy of 40 cm^{-1}. Which one of the following statements about the coupling of vibrational and rotational motion is true? [NET-June 2011]

(a) The coupling is stronger in BX.
(b) The coupling is stronger in AX.
(c) Magnitude of coupling is same in both AX and BX.
(d) There is no coupling in both AX and BX

Soln. As per B.O. approximation we can consider the two different motions independent if their energy difference is large. In other words if energy difference of two different motions is large, the coupling between them will be minimum.

In case of AX the energy difference of vibrational and rotational energy is large compared to BX. Hence coupling will be stronger in BX.

Correct answer: (a)

4. The order of carbonyl stretching frequency in the IR spectra of ketone, amide and anhydride is:

(a) Anhydride > amide > ketone
(b) Ketone > amide > anhydride
(c) Amide > anhydride > ketone
(d) Anhydride > ketone > amide

Soln. Because $\upsilon_{C=O}$ of anhydride = 1800 –1900 cm^{-1}.

υ_{C-O} of ketone = 1720 cm^{-1}. υ_{C-O} of amide = 1600–1700 cm^{-1}.

Correct answer: (d)

5. In IR spectrum of $\left[Co(CN)_5H\right]^{3-}$ the Co–H stretch is observed at 1840 cm^{-1}. The (Co–I) stretch in $\left[Co(CN)_5D\right]^{3-}$ will appear at nearly [NET-June 2011]

(a) 1300 cm^{-1} (b) 1400 cm^{-1} (c) 1500 cm^{-1} (d) 1600 cm^{-1}.

Soln. As frequency of vibration $= \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$;

where k = force constant of bond
M= reduced mass.

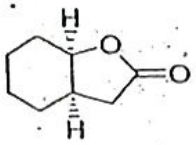
∴ Ratio of frequency/wave number of Co–D and Co–H bond is,

$$\frac{\bar{\upsilon}_{Co-D}}{\bar{\upsilon}_{Co-H}} = \sqrt{\frac{\mu_{Co-D}}{\mu_{Co-H}}} = \sqrt{\frac{\frac{60\times1}{61}}{\frac{60\times2}{62}}} = \frac{1}{\sqrt{2}}$$

$$\therefore \quad \bar{\upsilon}_{Co-D} = \bar{\upsilon}_{Co-H} / \sqrt{2} = \frac{1840}{\sqrt{2}} = 1300\ cm^{-1}$$

Correct answer: (a)

6. In the IR spectrum, carbonyl absorption band for the following compound appears at



[NET-Dec. 2011]

(a) 1810 cm^{-1} (b) 1770 cm^{-1} (c) 1730 cm^{-1} (d) 1690 cm^{-1}

Soln. C = O stretching frequency for simple ester 1750-1725 cm^{-1}.
For sixmembered lactone = 1735 – 1750 cm^{-1}.
For five membered lactone = 1795-1760 cm^{-1}.
Correct answer is (b).

7. The vibrational energy levels, $\upsilon'' = 0$ and $\upsilon' = 1$ of a diatomic molecule are separated by 2143 cm^{-1}. Its anharmonicity $(\omega_e x_e)$ is 14 cm^{-1}. The values of ω_e $(\text{in } cm^{-1})$ and first overtone (cm^{-1}) of this molecule are respectively.

[NET-Dec. 2011]

(a) 2143 and 4286 (b) 2157 and 4286 (c) 2157 and 4314 (d) 2171 and 4258

Soln. $\bar{\nu}_{0\to1} = \omega_e(1-2x_e)$

or, $2143\ cm^{-1} = \omega_e - 2\omega_e x_e$

or, $2143\ cm^{-1} = \omega_e - 2\times14\ cm^{-1}$

or $\omega_e = 2171\ cm^{-1}$

First overtone more number is given by,

$$\bar{\nu}_{0\to2} = 2\omega_e(1-3x_e) = 2\omega_e - 6\omega_e x_e = 2\times2171 - 6\times14 = 4258\ cm^{-1}$$

Correct answer is (d).

8. The following data were obtained from the vibrational fine structure in the vibronic spectrum of a diatomic molecule:

[NET-June 2012]

$$\omega_e = 512\ cm^{-1}, \omega_e x_e = 8\ cm^{-1}$$

where ω_e is the energy associated with the natural frequency of vibration and x_e is the anharmonicity constant. The dissociation energy (D_e) of the molecule is:

(a) 4096 cm^{-1} (b) 6144 cm^{-1} (c) 8192 cm^{-1} (d) 16384 cm^{-1}.

Soln. Dissociation energy $D_e = \dfrac{\omega_e}{4x_e}$ $\omega_e = 512\ cm^{-1}$, $\omega_e x_e = 8\ cm^{-1}$, $x_e = \dfrac{8}{512}$

$$D_e = \frac{512}{\frac{4\times8}{512}} = \frac{512\times512}{32} = 8192\ cm^{-1}$$

Correct answer is (c).

9. The absorption spectrum of O_2 shows a vibrational structure that becomes continuum at 56875 cm^{-1}. At the continuum, it dissociates into one ground state atom (O_g) and one excited state atom (O_e). The energy difference between O_e and O_g is 15125 cm^{-1}. The dissociation energy (in cm^{-1}) of ground state of O_2 is:

(a) $\frac{56875}{15125}$ (b) $\frac{15125}{56875}$ (c) 72000 (d) 41750 [NET-Dec. 2012]

Soln.

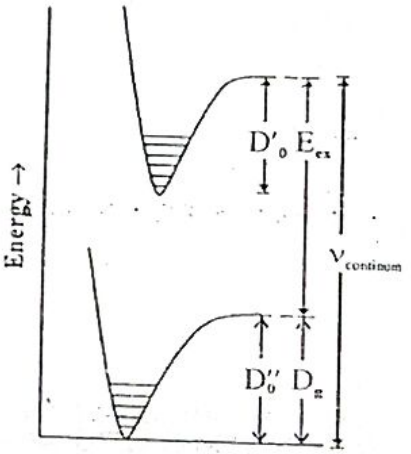


Illustration of dissociation

Dissociation energy, $D_g = 56875 - 15125 = 41750$

Correct answer is (d)

10. In the IR spectrum of p-nitrophenyl acetate, the carbonyl absorption band appears at

(a) 1670 cm^{-1} (b) 1700 cm^{-1} (c) 1730 cm^{-1} (d) 1760 cm^{-1}. [NET-Dec. 2012]

Soln. C = O structure occurs at cm^{-1}.

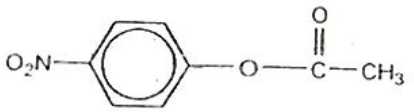
1750 – 1735 for aliphatic esters.

1740 – 1715 if C = O conjugated with aromatic.

1765 – 1762 if oxygen atom is conjugated with alkene or aromatic.

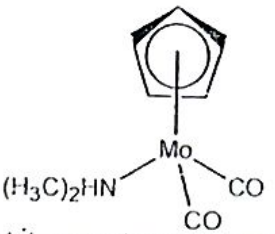
e.g. Phenyl acetate 1765 cm^{-1}

p-nitrophenyl acetate 1761 cm^{-1}.



Correct answer is (d)

11. For the molecule below, [NET-Dec. 2012]



consider the following statements about its room temperature spectral data.

(A) 1H NMR has singlets at 5.48 and 3.18 ppm

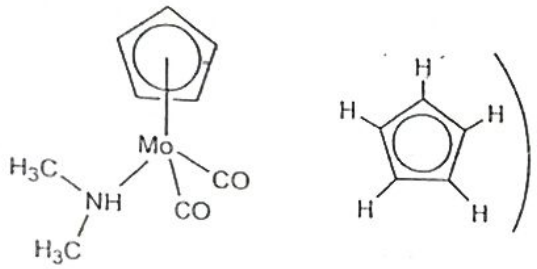
(B) 1H NMR has multiplet at 5.48 and singlet at 3.18 ppm

(C) IR has CO stretching bands at 1950 and 1860 cm^{-1}

(D) IR has only one CO stretching band at 1900 cm^{-1}.

The correct pair of statement is,
(a) A and C (b) B and C (c) A and D (d) B and D.

Soln.



all 5H proton gives on signal in ^1H NMR at 5.48

Since, the molecule is C_2–symmetric. So, two CO's will give two absorption band in IR spectrum
Correct answer is (a)

12. The vibrational frequency and anharmonicity constant of an alkali halide are 300 cm^{-1} and 0.0025 respectively. The positions (in cm^{-1}) of its fundamental mode and first overtone are respectively.
(a) 300, 600 (b) 298.5, 595.5 (c) 301.5, 604.5 (d) 290, 580 **[NET-Dec. 2012]**

Soln. $\omega_e = 300\ cm^{-1}$; $X_e = 0.0025$

Fundamental mode $= \omega_e(1-2X_e)$

First overtone $= 2\omega_e(1-3X_e)$

Fundamental $= 300(1-2\times0.0025) = 300\,(1-0.0025) = 300\times0.995 = 298.5$

First overtone $= 2\times300\,(1-3\times0.0025) = 600(1-0.0075) = 595.5$

Correct answer is (b).

13. A hypothetical molecule XY has the following properties
Reduced mass: 2×10^{-26} kg
X–Y bond length: 100 pm
Force constant of the bond: $8\times10^{2}\ N.m^{-1}$
(A) The frequency of radiation (in cm^{-1} units) required to vibrationally excite the molecule from v = 0 to v = 1 state is
(a) 3184.8 (b) 2123.2 (c) 061.6 (d) 840.0

Soln. ΔE = v = 0 to v = 1

$\Delta E = h\nu$ (for SHO)
$h\nu$ in joule

$$\frac{h\nu}{hc} = \frac{\nu}{c}\ cm^{-1} \qquad \Rightarrow \bar{\nu} = \frac{\nu}{c} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

$$\text{Wave number} = \frac{1}{2\pi\times3\times10^{10}\ cm/sec}\sqrt{\frac{8\times10^{2}\ N.m^{-1}}{2\times10^{-26}\ kg}} = \frac{1}{2\pi\times3\times10^{10}\ cm/sec}\sqrt{\frac{8\times10^{2}\ kg\ mtr\ mtr^{-1}}{2\times10^{-26}\ sec^{2}+kg}}$$

$$= \frac{1}{2\times3.14\times3\times10^{10}\ cm/sec}\frac{1}{sec}\sqrt{\frac{8\times10^{2}}{2\times10^{-26}}}$$

$$= \frac{2\times10^{14}}{6\times3.14\times10^{10}} = \frac{10000}{9.14} = 1061.4$$

(B) The frequency of radiation (in cm^{-1} units) required to rotationally excite the molecule from J = 0 to J = 1 state is

(a) 1.4 (b) 2.8 (c) 3.2 (d) 3.6

Soln. J = 0 to J = 1

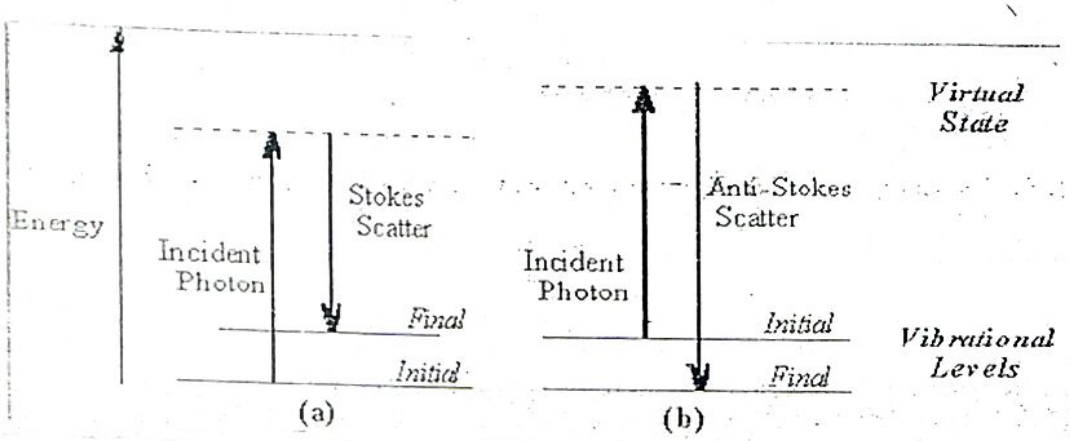
$2B =$ $\quad B = \frac{h}{8\pi^2 IC}$

$$= \frac{2\times h}{8\pi^2 IC} = \frac{2\times6.6\times10^{-34}\ J.s}{8\times3.14\times3.14\times2\times10^{-26}\times3\times10^{10}\ cm/s\times100\times10^{-12}\ mtr\times100\times(-1.2)mtr}$$

$$= \frac{2\times6.6\times10^{6}}{8\times3.14\times3.14\times2\times3} = \frac{2\times6.6\times10^{2}}{473.2} = \frac{1320}{413} = 2.8$$

RAMAN SPECTROSCOPY

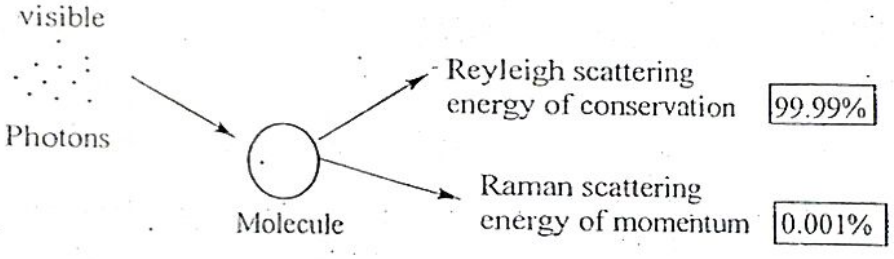
The Raman effect arises when a photon is incident on a molecule and interacts with the electric dipole of the molecule. It is a form of electronic (more accurately, vibronic) spectroscopy, although the spectrum contains vibrational frequencies. In quantum mechanics the scattering is described as an excitation to a virtual state lower in energy than a real electronic transition with nearly coincident de-excitation and a change in vibrational energy. The scattering event occurs in 10-14 seconds or less.

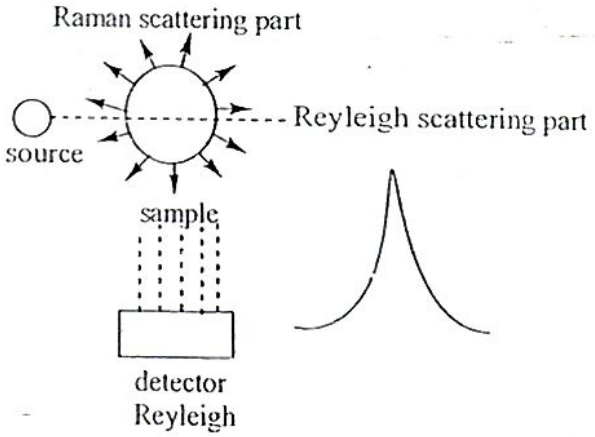


Energy level diagram for Raman scattering; (a) Stokes Raman scattering (b) anti-Stokes Raman scattering.

structural information form scattering property of molecule :

SCATTERING OF PHOTONS :





Source, sample and detector are situated at 90° of each other.

Configuration of source sample detector :

(1) All absorption spectroscopy = linear Source → Sample → detector.

(2) Raman and all emission spectroscopy = 90° S —— D
|
S

Laser Source : Having more no. of photon per unit volume.

Raman spectroscopy gives specially information of biological sample (biomolecule) because biological sample contain water. Water is not Raman scattering while in I.R. H_2O absorb photon.

RAMAN ACTIVITY : In order to the Raman active a molecular rotation or vibration must cause some change in a component of molecular polarisability.

The change in molecular polarisability may be change in direction or change in magnitude.

Molecular polarisability is an anisotropic property and may be defined as

$$\boxed{\mu = \alpha E}$$

α = Polarisability

E = Electric field of radiation

μ = induced dipole moment.

Polarisability ellapsoid is defined as 3 dimensional surface whose distance from the electrical centre of molecule is directly proportional to $\frac{1}{\sqrt{a_i}}$ where a_i = polarisability along the line joining a point i with electric centre.

All the molecules having centre of symmetry shows mutual exclusion between I.R. activity and Raman activity. If the molecule has centre of symmetry then its IR active vibrations will be Raman inactive and Raman active vibration will be IR inactive.

Problem. Classify the molecules as microwave, I.R. & Raman active molecules?

	Molecule	Rotational Microwave	I.R	Raman
1.	$CH_2 = CH_2$ symmetrical top (have parmament dipole)	Inactive	Active	Active
2.	SO_2 assymmetric top	active	Active	Active
3.	H_2, Cl_2, O_2 Homodiatomic mole	Inactive having no dipole	Inactive no dipole change	Inactive
4.	CO_2	inactive	Active (asymmetric strech)	Active (symmetric strech)
5.	CH_4 (Spherical top having no centre of symmetry	inactive	active	active
6.	SF_6	Inative	Inative	Inative
7.	HCl Heterodiatomic molecule	Active	Active	Active
8.	ClF_3	active	active	active

CO_2 MOLECULE :

(1) Rotational Inactive :

(2) I.R. Active :

Symmetric Strech – I.R. active

Asymmetric strech – I.R. active

Bend – I.R. active

(3) Raman Active

Symmetric strech – I.R. active

Asymmetric strech – I.R. inactive

Bend – Raman inactive

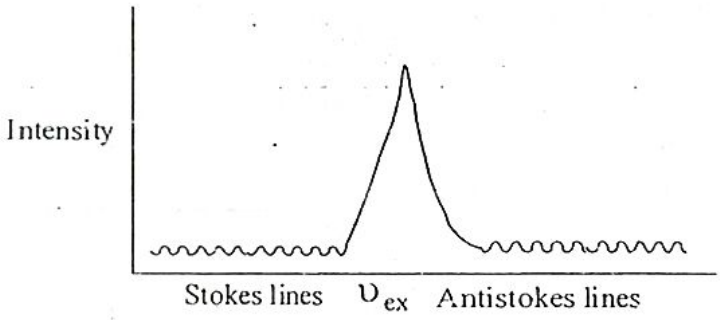
RAMAN EFFECT AND RAMAN SCATTERING

When a electromagnetic radiation of frequency υ consisting a stream of photon having energy $h\upsilon$ strikes the molecule of sample then two possibilities are there

(1) If the collision is perfectly elastic then the photon will deflect as such without energy change.
This scattering of photon is known as Reyleigh scattering.

(2) If the collision is inelastic then the molecule can gain or loss energy related to the rotational and vibrational energy levels.
This scattering is known as Raman Scattering
If the molecules gain energy ΔE then the photon will be scattered with energy $h\upsilon - \Delta E$. Where ΔE is the Raman shift.
The value of Raman shift ΔE will be equal to the separation in rotational energy levels in pure rotational Raman spectra.
The value of Raman shift will be equal to the separation in vibrational energy levels. If in the vibrational Raman spectra.

The radiation scattering with a frequency lower than that of incident frequency is known as stokes radiation.
Radiation scattered with a frequency higher than that of incident frequency is known as Antistoke radiation.



Since the population in the ground state of vibrational and rotational energy levels are always higher than exited state.
In the Raman scattering if the photons is scattered by a ground state molecule then it loses the energy equivalent to rotational or vibrational energy level separation and scattered photon has energy less than incident photon. This is stoke radiation.
Scattered photon has higher energy than incident photon. This is antistoke radiation.
Since the population of molecules in the ground state of rotational and vibrational energy levels are always higher than that of exited state Hence the intensity of stoke lines will be always higher than antistokes lines.
The position of stoke and antistokes lines are mirror image of each other from the position of incident radiation.

Quantum Theory of Raman Effect:

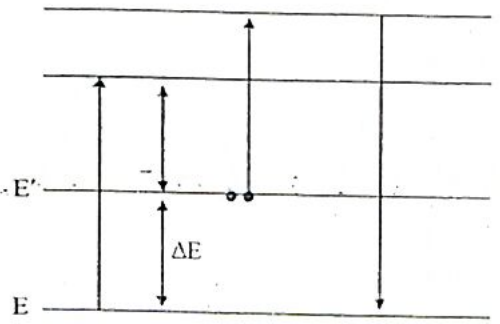
Raman effect can be explain by quantum theory when light fall on scattered the photon collide with the molecule of scattered.

There are three possibility of collision.

(i) Collision may be elastic

(ii) Collision may be ielastic in which molecule in its initial energy.

E"(GS) take energy from photon and goes to higher energy state and the photon is scattered with small energy.



If $h\nu = 122\ cm^{-1}$

$h\nu - \Delta E = 120\ cm^{-1}$

$$\boxed{\Delta E = E' - E''}$$

This gives to Raman line which freuquency lower than that of incident spectral line at a wave number.

$$= \frac{hc\bar{\nu} - \Delta E}{hc}$$

The wave number shift $\frac{\Delta E}{hc}$ is called as strokes line. (decreased Raman line is strokes line)

$$= \frac{hc\bar{\nu}}{hc} - \frac{\Delta E}{hc} \qquad \Rightarrow \bar{\nu} - \frac{\Delta E}{hc}$$

The photon may collide with a scattered molecule already in the excitted energy state E' and take ΔE from it. In this case the molecule is deexcited to the ground state E" and the photon is scattered with energy $hc\bar{\nu} + \Delta E$. This given rise to Raman line with frequency higher than that of incident spectral line

$$\frac{hc\bar{\nu} + \Delta E}{hc}$$

Antistrokes lines is weaker than the strokes line because in excited state the number of molecule is very small chance of the collision is very small. The energy ΔE which is add or given up of the molecule may be of the order vibrational energy and rotational energy on the basis of which we decide rotational Raman or vibrational Raman.

PURE ROTATIONAL RAMAN SPECTRA (For linear mole.) :

$$\epsilon_J = BJ(J+1) - DJ^2(J+1)^2\ cm^{-1}$$

This is the energy level equation for the linear molecule. If we ignore the D then $\epsilon_J = BJ(J+1)\,cm^{-1}$

Selection Rule :

$$\Delta J = 0, \pm 2$$

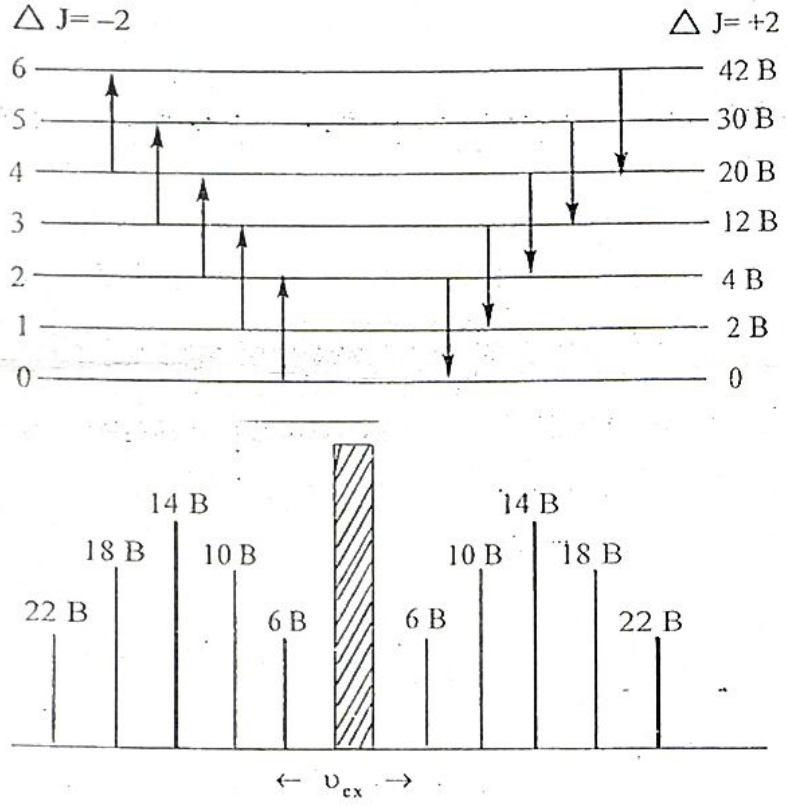
$\Delta J = 0$ means no rotation, no change in the energy of photon.

In the rotational spectrum the selection rule was $\Delta\bar{J} = \pm 2$ this is because during $\frac{m}{n}$ rotation the polarisability ellipsoid presence the same appearance two times in acomplete rotation.

Calculation $J \rightarrow J+2$

$$\epsilon_{J+2} - \epsilon_J = B(J+2)(J+2+1) - BJ(J+1)$$

$$\epsilon_{J+2} - \epsilon_J = B(4J+6)\ cm^{-1}$$



$\Delta J = B(4J+6)$

$J = 0 \Rightarrow 6\ B$ $\quad$ $J = 3 \Rightarrow 18\ B$

$J = 1 \Rightarrow 10\ B$ $\quad$ $J = 4 \Rightarrow 22\ B$

$J = 2 \Rightarrow 14\ B$

$$\boxed{\text{Raman shift} = \upsilon_{ex} \pm \beta(4J+6)}$$

For (–) Stoke lines

(+) Antistoke lines

SYMMETRIC TOP MOLECULES :

$$\boxed{\epsilon_{JK} = BJ(J+1) - (A-B)K^2 \ \ cm^{-1}}$$

Selection Rule

$\Delta K = 0$; $\Delta J = 0, \pm 1$ and ± 2 only

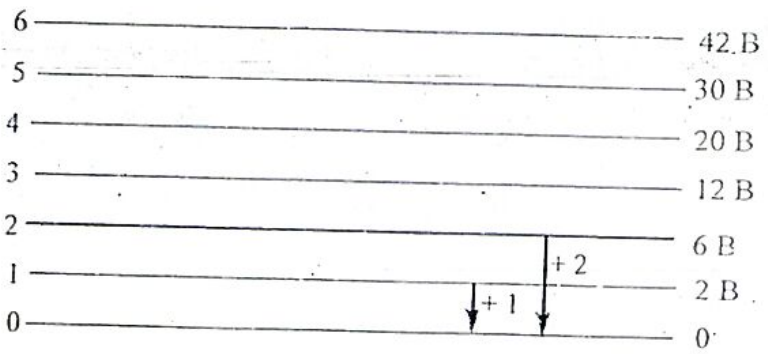
$\pm 1 \rightarrow$ R lines $\begin{cases} -1 & \text{R-stokes} \\ +1 & \text{R-Antistokes} \end{cases}$

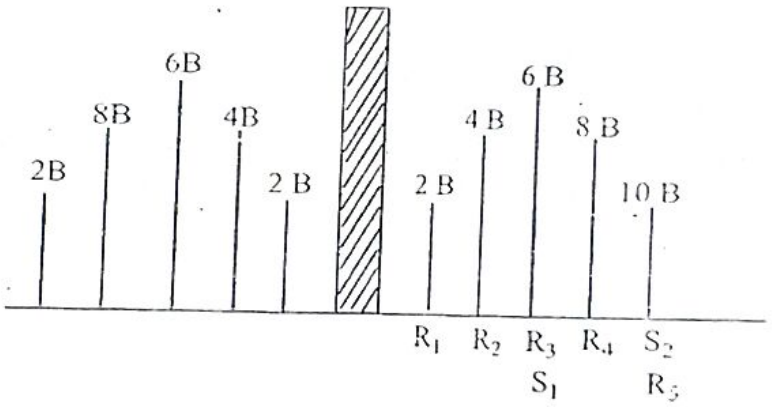
$\pm 2 \rightarrow$ S lines $\begin{cases} -2 & \text{S-stokes} \\ +2 & \text{S-Antistokes} \end{cases}$

$\Delta J = \pm 1$

for $\Delta E_{JK} = 2B(J+1)\ cm^{-1}$

for $\Delta J = \pm 2 \quad \Delta \epsilon_{JK} = B(4J+6)\ cm^{-1}$





for +1
$J = 0 \Rightarrow 2B$
$J = 1 \Rightarrow 4B$
$J = 3 \Rightarrow 8B$
$J = 4 \Rightarrow 10B$

for +2
$J = 0 \Rightarrow 6B$
$J = 1 \Rightarrow 10B$
$J = 2 \Rightarrow 14B$
$J = 3 \Rightarrow 18B$

VIBRATIONAL RAMAN SPECTRA

$$E\upsilon = \left(\upsilon + \frac{1}{2}\right)\bar{\omega}e - x_e\bar{\omega}e\left(\upsilon + \frac{1}{2}\right)^2 cm^{-1}$$

Selection Rule : $\Delta\upsilon = 0, \pm 1, \pm 2...$

For $\Delta\upsilon = \pm 1$

$\Delta_{e\upsilon} = \omega_e(1 - 2x_e)$

Raman shift $= \upsilon_{ex} \pm \omega_e(1 - 2x_e)$

ROTATIONAL VIBRATIONAL RAMAN SPECTRA OR, RAMAN SPECTRUM OF ROTATING VIBRATOR

$$\boxed{\in_{J\upsilon} = \left(\upsilon + \frac{1}{2}\right)\bar{\omega}e - x_e\bar{\omega}e\left(\upsilon + \frac{1}{2}\right)^2 + BJ(J+1)\,cm^{-1}}$$

Selection Rule : $\Delta J = 0, \pm 2$

$\Delta\upsilon = \pm 1, \pm 2, \pm 3.....$

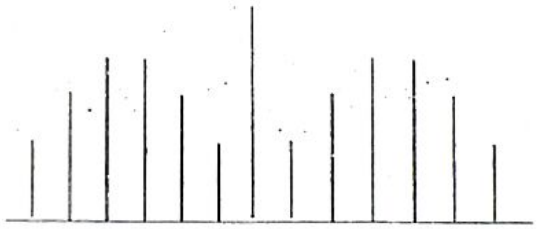
For $\Delta H = \pm 2$

$\Delta\upsilon = \pm 1$

$\upsilon = 0$ to $\upsilon = 1$

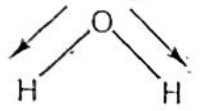
Then

$\Delta J = +2$	$\Delta \in = \omega_e^- + B(4J+6)$	S lines
$\Delta J = -2$	$\Delta E = \omega_e^- - B(4J+6)$	O lines
$\Delta J = 0$	$\Delta E = \omega_e^-$	Q lines



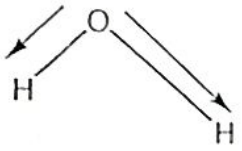
Raman shift $= \pm\left[\omega_e \pm B(4J+6)\right]$

POLARISATION OF RAMAN LINES : When the incident radiation in the Raman spectroscopy is plane polarised light (pp laser) then after scattering the two types of Raman scattering photon can be observed. The Raman scattered photon comming from scattering with



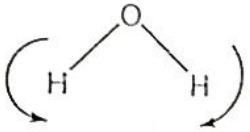
C_2V

Symmetric strech



C_2V change into Cs

assymmetric strech

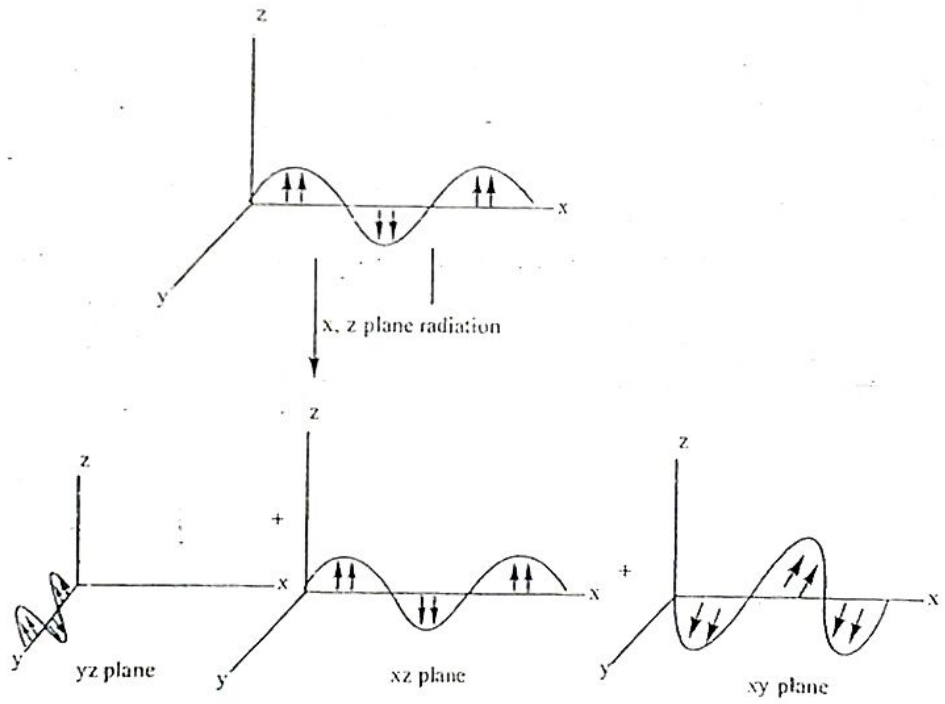


C_2V

a symmetric vibration remains plane polarised as such

But the photon strikes to the assymmetric vibration become depolarised to some extent that depend on the assymmetry of the vibration. The degree of depolarisation of Raman scattered photon can be measure as depolarisation ratio of the particular Raman line that is equal to the intensity of perpendicular is photon.

$$\rho = \frac{I_{\perp} \text{ photon}}{I_{\parallel} \text{ photon}}$$



Total symmetry $I_{\perp} = 0$, $I_{\parallel} = 1$

Total assymmetric $I_{\perp} = 1$, $I_{\parallel} = 0$

$\rho = 0 \rightarrow 1$ · means

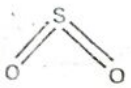
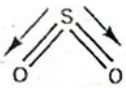
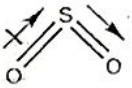
$$\left.\begin{matrix} I_{\perp} = 0 \\ I_{II} = 1 \end{matrix}\right\} \int = 0 \qquad \left.\begin{matrix} I_{\perp} = 1 \\ I_{II} = 0 \end{matrix}\right\} \rho = 1$$

If the value of $\rho \geq 3/4$ the line will be depolarised then it is assymmetric vibration.

$\rho < 3/4$ line polarised then symmetry vibration.

I.R. AND RAMAN BAND FOR SO_2 :

		I.R.	Raman	
1.	$519\,cm^{-1}$	II type	Polarise	Bending
2.	$1151 cm^{-1}$	II type	Polarise	Symmetric
3.	$1361 cm^{-1}$	⊥type	depolarise	Assymmetric

(1)  bending (2)  symmetric (3)  assymmetric

INTENSITY ALTERNATION IN ROTATIONAL RAMAN SPECTRA

The rotational Raman spectra of 'homonuclear' diatomic molecules show an intensity alternation, just as the electronic bands of these molecules show, Again, this is due to the alternating nuclear-spin statistical weight of the rotation levels. Let us consider a few specific cases of H_2, D_2, N_2, O_2 and C_2.

Note: Odd and even lines are based on odd and even J values respectively from which transition is taking place.

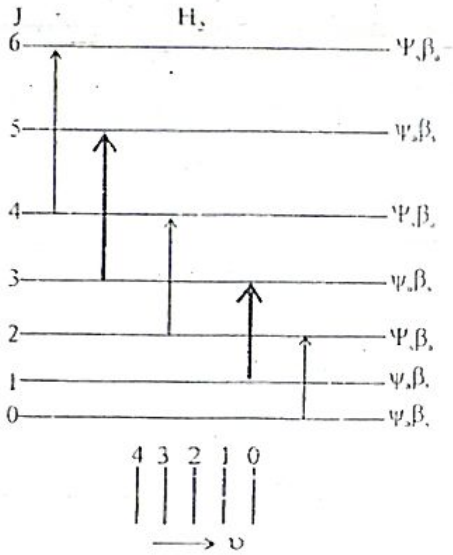
Example: For $\Delta J = +2$ (S lines)

$J = 0$ to $J = 2$ transition with be 0^{th} line and designated as S(0) (even line).
$J = 1$ to $J = 3$ transition will be I^{st} line and designated as S(1) (odd line).
$J = 7$ to $J = 9$ transition is S(7) line and it is an odd line.

For $\Delta J = -2$ (0 lines)

$J = 2$ to $J = 0$ transition is O(2) line (even line)
$J = 3$ to $J = 1$ transition is O(3) line (odd line).

H_2 : A hydrogen nucleus has a spin given by $I = \frac{1}{2}$.



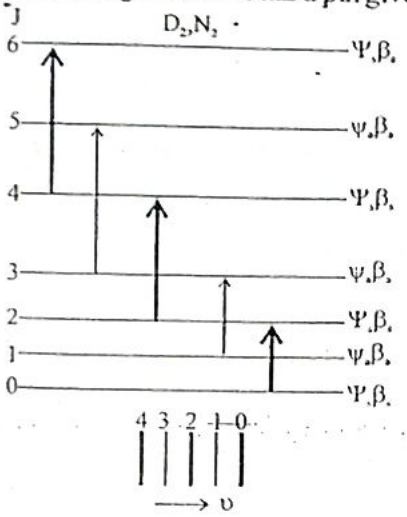
$^1\Sigma_g^+ \left(I = \frac{1}{2} \right)$

The population ratio of rotation levels (= Statistical weight ratio = Intensity ratio) =

$$\frac{\text{odd} - J}{\text{even} - J} = \frac{N_s(\beta_s)}{N_a(\beta_a)} = \frac{1+1}{1} = \frac{(1/2)+1}{1/2} = \frac{3}{1}.$$

The rotational Raman transitions corresponding to stokes lines and the resulting spectrum are shown in (The numbers written at the top of the spectral lines represent J value of the lower level involved). the odd-J lines must be three times as strong as the even-J lines, ignoring Boltzmann intensity variation. This is found in agreement which experiment.

D_2 and N_2: A heavy-hydrogen or nitrogen nucleus has a pin given by $I = 1$.



$^1\Sigma_g^+ (I = 1)$

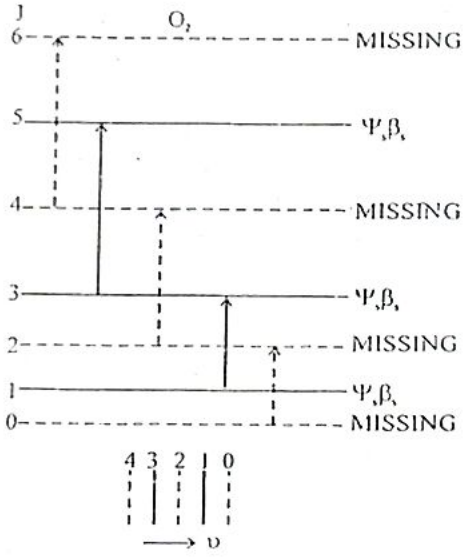
The population ratio of the rotational levels is

$$\frac{\text{even} - J}{\text{odd} - J} = \frac{N_s(\beta_s)}{N_a(\beta_a)} = \frac{I+1}{I} = \frac{I+1}{1} = \frac{2}{I}$$

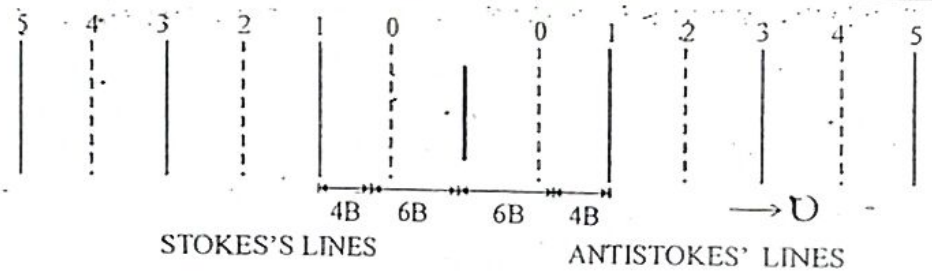
In the rotational Raman spectrum, therefore the even-J lines must be twice as strong as odd-J lines (Fig.7) this is actually found to be the case which confirms that the nuclei of D_2 and N_2 have a spin $I = 1$ and follow Bose-Einstein statistics.

O_2 or C_2: The oxygen nucleus has a spin, $I = 0$ and is a boson.

In this case even J lines will be missing.



$^3\Sigma_g^- (I = 0)$



There are three possibilities :

(i) if no line is missing then the ratio

$$\frac{\text{separation between first Stock and first anti-stockes lines}}{\text{separation between successive line in either branch}} = \frac{12\,B}{4\,B} = \frac{6}{2}$$

(ii) If even-J lines are missing, then above ratio is 20B/8 B = 5:2 and

(iii) If odd-J lines are missing the ratio is 12B/8B = 3 : 2

Therefore without knowing B, we decide with which case we are dealing. In case of Raman spectrum of O_2, C_2 this ratio is experimentally found to be 5:2. Hence we can conclude that even-J lines are missing.

SOLVED PROBLEMS

1. What are the relative populations of alternate rotational levels of $^1\sum_g^+$ states for $B_2, O^{17}\,O^{17}$ and O^{17} molecules ? Ignore Boltzmann factors. Nuclear spins of B and O^{17} and 3 and $\frac{5}{2}$ respectively.

Soln. The spin of each nucleus of B_2 is I = 3.

Therefore, the ratio of the nuclear-spin statistical weight of the symmetric and antisymmetric spin states is

$$\frac{N_s(\beta_s)}{N_a(\beta_a)} = \frac{I+1}{I} = \frac{4}{3}.$$

The nuclei are bosons (I integral), and so the symmetric nuclear-spin states (β_s) are associated with symmetric rotational states (ψ_s) and β_a states are associated with ψ_a states, so that the complete molecular wavefunction is symmetric.

For the state $^1\sum_g^+$ (even and positive), the even-J levels are symmetric (ψ_s) and the odd-J levels are antisymmetric (ψ_a). Hence the population ratio of even-numbered to odd-numbered rotational levels is

$$\frac{\text{even} - J(\psi_s\beta_s)}{\text{odd} - J(\psi_a\beta_a)} = \frac{N_s}{N_a} = \frac{4}{3}$$

The spin of each nucleus of $O^{17}\,O^{17}$ is $I = \frac{5}{2}$.

In this case, we have, $\frac{N_s(\beta_s)}{N_a(\beta_a)} = \frac{I+1}{I} = \frac{7}{5}$.

The nuclei are now fermions (I half-integral), and so the complete molecular wavefunction must be antisymmetric with respect to the nuclei. Hence the possible combinations of coordinate and nuclear-spin wavefunction are $\psi_s\beta_a$ and $\psi_a\beta_s$.

Again for the state $^1\sum_g^+$, the even-J levels are symmetric (ψ_s) and the odd-J levels are antisymmetric (ψ_a). Therefore, $\frac{\text{even}-J(\psi_s\beta_a)}{\text{odd}-J(\psi_a\beta_s)}=\frac{N_a}{N_s}=\frac{5}{7}$.

In case of isotopic molecule O^{16} O^{17}, the population is not affected by nuclear spin. It is governed by Boltzmann factor only.

2. What is the total degeneracy of the J=0,1 and 2 levels of the ground electronic state of (i) H_2, (ii) D_2, (iii) HD and (iv) C_2 molecules ?

Soln. The rotational levels of all diatomic molecules have a (2J+1) space-degeneracy.

The nuclear-spin statistical weight has the value $(2I_A+1)(2I_B+1)$ for all rotation levels of a heteronuclear or isotopic molecule, where I_A and I_B are the spins of the (different) nuclei of the molecule. In case of homonuclear molecules, however, the nuclear statistical takes different value for the symmetric and antisymmetric nuclear-spin states. If I is the spin of each of the two (identical) nuclei, then

$$N_s=(2I+1)(I+1) \quad \text{and} \quad N_a=(2I+1)I.$$

Hence the total degeneracy of the rotational levels of a heteronuclear molecule is $(2I_A+1)(2I_B+1)(2J+1)$; while for a homonuclear molecule it is $(2I+1)(I+1)(2J+1)$ for levels belonging to symmetric nuclear-spin states, and $(2I+1)I(2J+1)$ for levels belonging to antisymmetric spin states.

Let us now consider the given molecules.

(i) H_2 $\qquad I=\frac{1}{2}$ (Fermion)

In the ground state $^1\sum_g^+$ even-J levels are space-symmetric and odd-J levels are space-antisymmetric and are the stronger ones (because nuclei are fermions, $\psi'=\psi_s\beta_a, \psi_a\beta_s$). Hence the total degeneracies are :

for J = 0 ; $\quad (2I+1)\,I\times(2I+1)=1\times1=1,$
for J = 1; $\quad (2I+1)\,(I+1)\times(2J+1)=3\times3=9$
for J = 2; $\quad (2I+1)\,I\times(2J+1)=1\times5=5.$

(ii) D_2 : $\qquad I=1$ (boson).

In this case even-J levels are the stronger. Therefore,

for J = 0 ; $\quad (2I+1)\,(I+1)\times(2J+1)=6\times1=6,$
for J = 1; $\quad (2I+1)\,I\times(2J+1)=3\times3=9$
for J = 2; $\quad (2I+1)\,(1+1)\times(2J+1)=6\times5=30.$

(ii) HD : it is an isotopic molecule and so all rotational levels have the same nuclear-spin degeneracy $(2I_A+1)(2I_B+1)$. $\quad I_A=\frac{1}{2}, I_B=1,$

Thus we have

for J = 0 ; $\quad (2I_A+1)(2I_B+1)\times(2J+1)=6\times1=6,$

for J = 1; $\quad (2I_A+1)(2I_B+1)\times(2J+1)=6\times3=18,$

for J = 2; $\quad ((2I_A+1)(2I_B+1)\times(2J+1)=6\times5=30,$

(iv) C_2 : $I = 0$ (boson).

For C_2, the ground electronic state is $^3\Pi_u (\Lambda = 1)$. In this state the level J = 0 does not exist

All other levels J = 1, 2 have Λ-doubling, but for $C_2 (I = 0)$ one of these components is missing. Thus the degeneracy of the appearing components is given by :

for J = 1; $(2I + 1)(I + 1) \times (2J + 1) = 3$

for J = 2; $(2I + 1)(1 + 1) \times (2J + 1) = 5$.

3. For the vibrational Raman spectrum of a homonuclear diatomic molecule, the selection rule under harmonic approximation is **[NET-June 2012]**

(a) $\Delta v = 0$ only (b) $\Delta v = \pm 1$ only (c) $\Delta v = \pm 2$ only (d) $\Delta v = 0, \pm 1$

Soln. For diatomic simple harmonic oscillator. All the vibrational energy levels are equally spaced and selected rule $\Delta \bar{v} = \pm 1$ only.

Correct answer is (b).

4. The rotational constant of $^{14}N_2$ is 2 cm^{-1}. The wave number of incident radiation in a Raman spectrometer is 20487 cm^{-1}. What is the wave number of first scattered Stokes line (in cm^{-1}) of $^{14}N_2$?

(a) 20479 (b) 20475 (c) 20499 (d) 20495 **[NET-June 2011]**

Soln. In Raman Spectra, Stokes lines are seperated by 4 B cm^{-1} and have wave number value less than the incident radiation, but the first Stoke's line is obsorbed at $\bar{\upsilon} - 6B$

$\therefore$ $6B = 6 \times 2\ cm^{-1} = 12\ cm^{-1}$

$\therefore$ Ist Stoke line wave number = wave number of incident $- 12 cm^{-1}$ radiation.

$= (20487 - 12)\ cm^{-1} = 20475\ cm^{-1}$

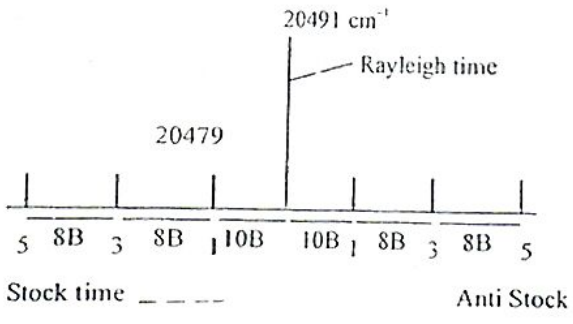
Correct answer: (b)

5. A 20491 cm^{-1} laser line was used to excite oxygen molecules (made of ^{16}O only) to obtain the rotational Raman spectrum. The resulting rotational Raman spectrum of oxygen molecule has the first Stokes line at 20479 cm^{-1}.

(A) The rotational constant (usually denoted as B) for the oxygen molecule is

(a) 1.2cm^{-1} (b) 2.0 cm^{-1} (c) 3.0 cm^{-1} (d) 6.0 cm^{-1}

Soln. A 20491 cm^{-1} laser line was used to excite oxygen molecule because molecule made ^{16}O only because molecule have spin zero. In the spin zero molecule even J line are missing in Raman spectrum. e.g. O_2, CO_2.



Rotational constant $B = \frac{20491 - 20479}{} = 12$

$10\ B = 12$

$B = 1.2\ cm^{-1}$

(B) The next rotational Stokes line is expected at

(a) 20467 cm^{-1} (b) 20469 cm^{-1} (c) 20471 cm^{-1} (d) 20475 cm^{-1}

Soln. The next rotational stoke time is first stokes time is 20479

Second time difference is 8B

$B = 1.2$

$8 \times 1.2 = 9.6$

So, second stock time is $20479 - 9.6 = 20469.7\ cm^{-1}$.

Correct answer is (b)

The electronic spectra of diatomic molecules:

(a) Term symbols: The term symbols of linear molecules (the analogoues of the symbols ^2P, etc. for atoms) are constructed in a similar way to those for atoms, but attention must be paid to the component of total orbital angular momentum about the internuclear axis, $\Lambda\hbar$. The value of $|\Lambda|$ is denoted by the symbols $\Sigma, \Pi, \Delta, ...$ for $|\Lambda| = 0, 1, 2.....$, respectively.

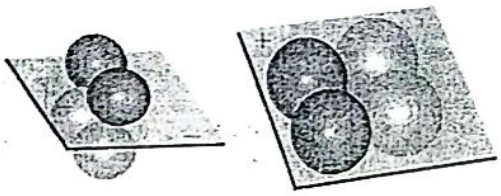


Fig-1. The + or – on a term symbol refers to the overall symmetry of a configuration under reflection in a plane containing the two nuclei.

These labels are the analogous of S, P, D, ... for atoms. The value of Λ is the sum of the values of λ, the quantum number for the component $\lambda\hbar$ of orbital angular momemtum of an individual electron around the internuclear axis. A single electron in a σ orbital has $\lambda = 0$: the orbital is cylindrically symmetrical and has no angular nodes when viewed along the internuclear axis. Therefore, if that is the only electron present, $\Lambda = 0$. The term symbol for H_2^+ is therefore Σ.

As in atoms, we use a superscript with the value of $2S + 1$ to denote the multiplicity of the term. The component of total spin angular momentum about the internuclear axis is denoted Σ, where Σ=S, S–1, S-2, ...,-S. For H_2^+, because there is only one electron, $S = s = \frac{1}{2}\left(\Sigma = \pm\frac{1}{2}\right)$ and the term symbol is $^2\Sigma$, a doublet term. The overall parity of the term is added as a right subscript. For H_2^+, the parity of the only occupied orbital is g. So, the term itself is also g, and in full dress is $^2\Sigma_g$. If there are several electrons, the overall parity is calculated by using.

$$\boxed{g \times g = g \qquad u \times u = g \qquad u \times g = u} \qquad \ldots (1)$$

These rules are generated by interpreting 'g' as +1 and u as –1. The term symbol for the ground state of any closed-shell homonuclear diatomic molecule is $^1\Sigma_g$ because the spin is zero (a singlet term in which all electron paired), there is no orbital angular momentum from a closed shell, and the overall parity is g.

A π electron in a diatomic molecule has one unit of orbital angular momentum about the internuclear axis $(\lambda = \pm 1)$, and if it is the only electron outside a closed shell, gives rise to a Π term. If there are two π electrons (as in the ground state of O_2, with configuration $1\pi_u^4\, 1\pi_g^2$) then the term symbol may be either Σ (if the electrons are travelling in opposite directions, which is the case if the occupy different π orbitals, one with $\lambda = +1$ and the other with $\lambda = -1$) or Δ (if they are travelling in the same direction, which is the case if they occupy the same π orbital, both $\lambda = +1$, for instance). For O_2, the two π electrons occupy different orbitals with parallel spins (a triplet term), so the ground term is $^3\Sigma$. The overall parity of the molecule is:

$$(\text{closed shell}) \times g \times g = g$$

The term symbol is therefore $^3\Sigma_g^-$.

Table: Properties of O_2 in its lower electronic states.

Configuration	Term	Relative energy/cm^{-1}	$\tilde{\nu}$ / cm^{-1}	R_e/pm
$\pi_u^2\pi_u^2\pi_g^1\pi_g^1$	$^3\Sigma_g^-$	0	1580	120.74
$\pi_u^2\pi_u^2\pi_g^2\pi_g^0$	$^1\Delta_g$	7 882.39	1509	121.55
$\pi_u^2\pi_u^2\pi_g^1\pi_g^1$	$^1\Sigma_g^+$	13 120.9	1433	122.68
$\pi_u^2\pi_u^1\pi_g^2\pi_g^1$	$^3\Sigma_u^+$	35 713	819	142
$\pi_u^2\pi_u^1\pi_g^2\pi_g^1$	$^3\Sigma_u^-$	49 363	700	160

For Σ terms, a $\pm$ superscript denotes the behaviour of the molecular wavefunction under reflection in a plane containing the nuclei (**Fig.-1**). If, for convenience, we think of O_2 as having one electron in $1\pi_{g,x}$, while changes sign under reflection in the yz-plane, and the other electron in $1\pi_{g,y}$, which does not change sign under reflection in the same plane, then the overall reflection symmetry is:

$$(\text{closed shell})\times(+)\times(-)=(-)$$

and the full term symbol of the ground electronic state of O_2 is $^3\Sigma_g^-$.

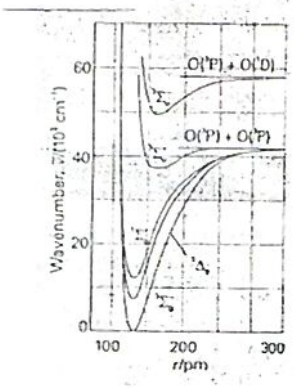


Fig-2. The electronic states of dioxygen.

The term symbols of excited electronic states are constructed in a similar way. For example, the term symbol for the excited state of O_2 formed by placing two electrons in a $1\pi_{g,x}$ (or in a $1\pi_{g,y}$) orbital is $^1\Delta_g$ because $|\Lambda|=2$ (two electrons in the same $\pi-$orbital), the spin is zero (all electrons are paired), and the overall parity is (closed shell) × g×g = g. **Table** and **Fig.-2** summarize the configurations, term symbols, and energies of the ground and some excited states of O_2.

(b) **Selection rules:** A number of selection rules govern which transitions will be observed in the electronic spectrum of a molecule. The selection rules concerned with changes in angular momentum are

$$\Delta\Lambda=0,\pm1 \quad \Delta S=0 \quad \Delta\Sigma=0 \quad \Delta\Omega=0,\pm1$$

where $\Omega=\Lambda+\Sigma$ is the quantum number for the component of total angular momentum (orbital and spin) around the internuclear axis (**Fig-3**). As in atoms, the origins of these rules are conservation of angular momentum during a transition and the fact that a photon has a spin of 1.

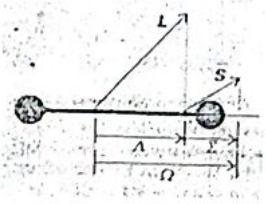


Fig-3. The coupling of spin and orbital angular momenta in a linear molecule: only the components along the internuclear axis are conserved.

There are two selection rules concerned with changes in symmetry. **First**, for Σ terms, only $\Sigma^+ \leftrightarrow \Sigma^+$ and $\Sigma^- \leftrightarrow \Sigma^-$ transitions are allowed. **Second**, the **Laprote selection rule** for centrosymmetric molecules (those with a centre of inversion) and atoms states that:

The only allowed transitions are transitions that are accompanied by a change of parity.

That is, u.→ g and g → u transitions are allowed, but g → g and u → u transitions are forbidden.

SOLVED PROBLEMS

1. Observe the following electronic transition of a diatomic molecule.

(a) ${}^1\Sigma_g^+ \rightarrow {}^3\Sigma_g^+$ (b) ${}^1\Sigma_u^+ \rightarrow {}^1\Sigma_g^+$ (c) ${}^1\Delta_u \rightarrow {}^1\Sigma_g^+$ (d) ${}^1\Pi_g \rightarrow {}^1\Sigma_u^+$

The allowed transitions are

(a) (A) and (C) only (b) (B) and (D) only (c) (A), (B) and (C) only (d) (A), (C) and (D) only

Soln. Selection rule for electronic transition

(i) $\Delta\Lambda = 0 \pm 1$, thus $\Sigma \longleftrightarrow \Sigma, \Sigma \longleftrightarrow \pi$(allowed) but $\Sigma \longleftrightarrow \Delta$ (not allowed)

(ii) $\Sigma^+ \longleftrightarrow \Sigma^+; \Sigma^- \longleftrightarrow \Sigma^-$; (allowed) but $\Sigma^+ \longleftrightarrow \Sigma^-$ (not allowed)

(iii) $\Delta S = 0$ thus ${}^1\Sigma \longleftrightarrow {}^1\Sigma$ (allowed) but ${}^1\Sigma \longleftrightarrow {}^2\Sigma$ (not allowed)

(iv) $g \longleftrightarrow u$(allowed) but $u \longleftrightarrow u$ and $g \longleftrightarrow g$(not allowed)

Correct answer is (b).

2. Which of the following electronic transitions are not allowed ? which rules are violated ?

(a) ${}^1\Sigma^+ - {}^1\Sigma^-$, (b) ${}^3\Sigma^+ - {}^1\Sigma^+$, (c) ${}^3u_u - {}^1\Sigma_u$, (d) ${}^1\Pi_g - {}^1\Sigma_u$, (e) ${}^2\Pi_{3/2} - {}^2\Sigma_{1/2}$.

Soln. (a), (b) , (c), (e) are not allowed.

(a) It violated the rule $\Sigma^+ \not\longleftrightarrow \Sigma^-$ (b) It violates the rule $\Delta S = 0$.

(c) It violates the rules $\Delta S = 0$, $\Delta\Lambda = 0 \pm 1$ and $g \longleftrightarrow u$. (d) It violates the rule $\Delta\Lambda = \Delta\Omega$.

3. Which of the following electronic transitions are allowed/not allowed? which rules are obeyed/violated.

(a) ${}^1\Sigma_u^+ - {}^1\Sigma_g^+$, (b) ${}^1\Sigma_g^- - {}^1\Sigma_u^+$ (c) ${}^3\Delta_u - {}^3\Pi_g$, (d) ${}^2\Sigma_u^+ - {}^2\Sigma_g^+$,

(e) ${}^1\Sigma_u^+ - {}^3\Sigma_g^-$, (f) ${}^3\Pi_g - {}^3\Delta_u$, (g) ${}^2\Pi_{3/2} - {}^2\Delta_{3/2}$, (h) ${}^3\Delta_1 - {}^3\Pi_2$.

Soln. (a) allowed (it obeys $\Delta S = 0, \Sigma^+ - \Sigma^+, u \longleftrightarrow g$)

(b) Not allowed (It violates $\Sigma^+ \not\longleftrightarrow \Sigma^-$ and $g \longleftrightarrow u$).

(c) allowed (It obeys $\Delta S = 0, \Delta\Lambda = 0 \pm 1$ and $u \longleftrightarrow g$)

(d) allowed, as (a).
(e) Not allowed. (It violates $\Delta S = 0$, $\Sigma^+ \longleftrightarrow \Sigma^-$).
(f) allowed, as (c)
(g) Not allowed. (It violates $\Delta\Lambda = \Delta\Omega$).
(h) Not allowed. (It violates $\Delta\Lambda = \Delta Q$).

4. The electric dipole allowed transition in a d^2 atomic system is **[NET-Dec.2012]**

(a) $^3F \rightarrow {}^1D$ (b) $^3F \rightarrow {}^1P$ (c) $^3F \rightarrow {}^3D$ (d) $^3F \rightarrow {}^3P$

Soln. Electric dipole allowed transition in d^2

For electronic transition selection rule, spin multiplicity $\Delta S = 0$; $\Delta\ell = \pm 1$, $\Delta J = 0, \pm 1$

$^3F \longrightarrow {}^3D$ allowed transition because $\Delta S = 0$, $\Delta\ell = -1$

Correct answer is (c)

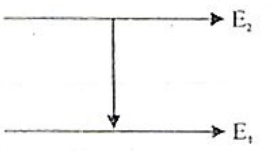
5. The relative population in two states with energies E_1 and E_2 satisfying Boltzmann distribution is given by $n_1/n_2 = (3/2)\exp\left[-(E_1 - E_2)/k_B T\right]$. The relative degeneracy g_2/g_1 is: **[NET-Dec.2012]**

(a) 2, (b) 2/3 (c) 3/2 (d) 3

Soln. The relative population in two states with energy E_1 and E_2 satisfy Boltzmann distribution law, $\frac{n_1}{n_2} = \frac{g_1}{g_2} e^{-\frac{[E_1 - E_2]}{kBT}}$

where, g_1 and g_2 are degeneracy $\frac{g_1}{g_2} = \frac{3}{2}$

The value of $\frac{g_2}{g_1} = \frac{2}{3}$



Correct answer is (b).

6. The Stark splitting for a given field is larger for a molecule AX as compared to BX. Which one of the following is true? (μ is the dipole moment) **[NET-June 2011]**

(a) $\mu_{AX} = \mu_{BX}$ (b) $\mu_{AX} > \mu_{BX}$ (c) $\mu_{AX} < \mu_{BX}$ (d) $\mu_{BX} = 2\mu_{AX}$

Soln.
- The degeneracy associated with the quantum number (M_J) (the orientation of the rotation in space) is partly removed when an electric field is applied on a polar molecule (eg. HCl, NH_3, etc)
- This splitting of states by an electric field is called Stark Effect.
- For any linear molecule (eg. AX or BX) in electric field (E), the energy of the state with quantum number J and MJ is given by,

$$E(J, M_J) = hc\, B \times J(J+1) + a(J, M_J)\mu^2 E^2$$

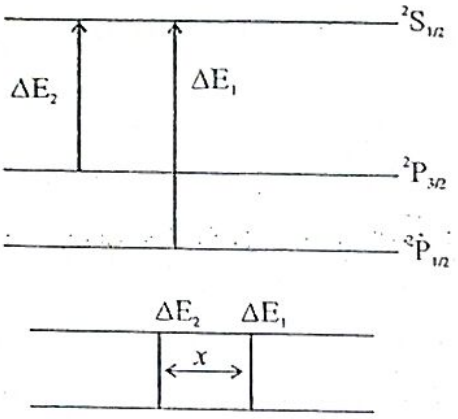
here energy depends on μ^2 (square of dipole moment), so large μ (dipole moment) will cause larger splitting. $\therefore \quad \mu_{AX} > \mu_{B}$

Correct answer: (b)

7. The sodium D lines are due to $^2P_{1/2} \rightarrow {}^2S_{1/2}(\Delta E_1)$ and $^2P_{3/2} \rightarrow {}^2S_{1/2}(\Delta E_2)$ transitions. The splitting due to spin-orbit coupling in ^2p state of the sodium atom is [NET-Dec. 2011]

(a) $\Delta E_2 + \Delta E_1$ (b) $\Delta E_2 - \Delta E_1$ (c) $\frac{\Delta E_2 + \Delta E_1}{2}$ (d) $\frac{\Delta E_2 - \Delta E_1}{2}$

Soln.



n = splitting due to spin orbital coupling = $|\Delta E_2 - \Delta E_1|$.

Correct answer is (b).